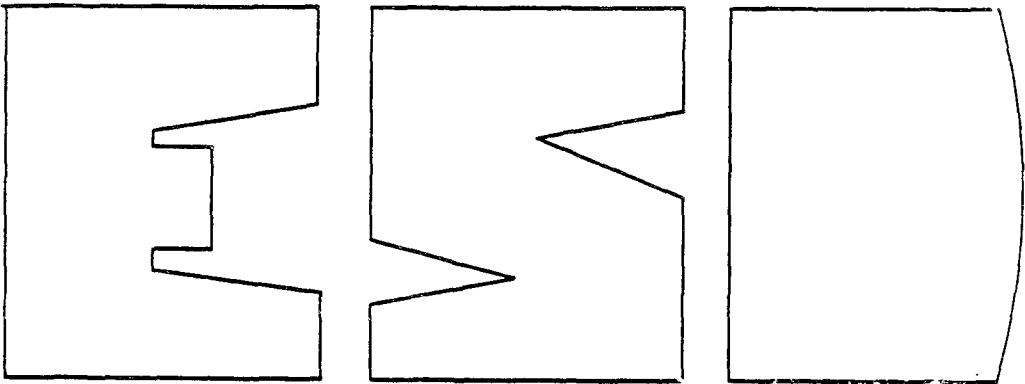
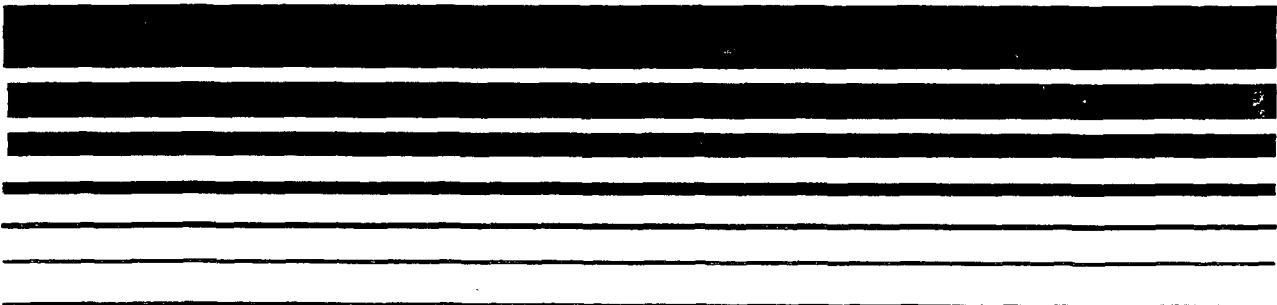




# Alternative Control Technology Document

## Control of VOC Emissions From the Application of Agricultural Pesticides





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## **Control of VOC Emissions from the Application of Agricultural Pesticides**

**Emission Standards Division**

**U. S. ENVIRONMENTAL PROTECTION AGENCY  
Office of Air and Radiation  
Office of Air Quality Planning and Standards  
Research Triangle Park, North Carolina 27711  
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## 1.0 INTRODUCTION

In the 1990 Clean Air Act Amendments, Sections 107 and 110 provide that each State has the primary responsibility to ensure that the air quality within the entire geographical area of the State meets national standards by submitting an implementation plan. This plan specifies the manner in which the National Ambient Air Quality Standards (NAAQS) will be achieved and maintained within each air quality control region of the State. If any region does not meet the NAAQS for a given pollutant, the area is designated as a nonattainment area. Each area designated as nonattainment for ozone, pursuant to Section 107, will be classified according to the degree of severity defined in Section 181 and a primary standard attainment date provided based on that classification. These attainment dates range from 3 years after enactment to 20 years after enactment.

In many States, some of the ozone nonattainment areas are comprised primarily of agricultural counties where a potentially significant contribution to the ozone may result from area sources of volatile organic compounds (VOC's) emissions. A potential source of VOC emissions in agricultural counties is the release of organic compounds from the application of agricultural pesticides. This report provides technical information that State and local agencies can consider while developing strategies for reducing VOC emissions. The focus of past work and study of VOC emission reduction from agricultural pesticide application has been on the solvent content in formulations of emulsifiable concentrates. In addition to reducing the VOC content in solvent-based liquid pesticides, reasonable control alternatives include reducing the use of organic fumigants and improving the

efficiency of application methods. In general, these control alternatives can be applied to agricultural pesticides; however, there may not be an alternative formulation for a given emulsifiable concentrate or a pesticide substitute for a fumigant in a certain situation.

An active ingredient in a synthesized pesticide is a VOC if it is an organic compound and the AI has the potential to be released into the atmosphere upon application. However, because the vapor pressure of active ingredients usually is very low and information on the fate of applied active ingredients usually is not available, there may be much uncertainty in actual versus potential emissions. In addition, it can be very difficult and costly to identify or develop a substitute active ingredient. This control option is perhaps the most undesirable. The information in this document will allow planners to (1) identify available alternative techniques for reducing VOC emissions from the agricultural application of pesticides; (2) determine the level of solvent VOC emissions and potential emission reductions; and (3) evaluate the cost and environmental impacts associated with implementing one or more of these techniques.

This document provides information on the total quantities of pesticides used nationwide and in ozone nonattainment areas, estimated VOC emissions and potential emission reductions, and estimated costs and implications associated with alternative techniques. Two methods are described for the determination of the organic solvent VOC content of pesticide formulations. The information presented in this document was obtained over 3 years through literature searches, existing pesticide data bases, and numerous discussions with EPA Office of Pesticide Programs personnel, State and county agricultural extension personnel, university agricultural personnel, pesticide manufacturers, industry trade associations, farm equipment manufacturers, and the California Air Pollution Control Officers Association (CAPCOA) Pesticides Solvents Task Force. Section 2.0 presents a summary of the findings of this study. Section 3.0 provides a description of the agricultural pesticide industry and the

processes emitting VOC's. Section 4.0 presents the estimated total quantities of the major active ingredients used and solvent VOC emissions from the agricultural application of pesticides on a nationwide basis and in ozone nonattainment areas. Section 5.0 discusses an array of VOC emission reduction techniques, the benefits and limitations of each technique, and the emission reduction potential. Sections 6.0 and 7.0 present a summary of the environmental impacts and the cost impacts, respectively, that may result from implementing the alternative control techniques. Section 8.0 discusses existing Federal and State regulations that apply to the pesticide industry. Appendix A presents a summary of the data base derived from the 1987 California Pesticide Use Report (PUR) and summary tabulations from the data base. Appendix B provides a summary of the data derived from the Resources for the Future data bases on nationwide herbicide and insecticide usage. Appendix C presents a summary of two analytical methods for determining the solvent VOC content of pesticide formulations.



## 2.0 SUMMARY

The purpose of this document is to provide technical information that State and local agencies can use to develop strategies for reducing volatile organic compound (VOC) emissions from the application of pesticides for agricultural purposes. Emphasis is placed on the solvent content of the pesticide formulation. This section presents the findings of this study including an estimation of solvent VOC emissions on a total nationwide basis and nationwide in ozone nonattainment areas, potential VOC reduction techniques based on the organic solvent content of the formulation, and the estimated solvent VOC emission reductions for each technique. Although emissions were not estimated for active ingredients, control techniques are discussed.

In most State and Federal laws, pesticides are termed economic poisons and are classified either according to the type of pest they are used to control or by their mode of action. Although there are more than 25 pesticide classes, the most widely used agricultural pesticides are herbicides and insecticides. These two classes compose approximately 80 percent of the total agricultural use of pesticides. The active ingredient in these pesticides is packaged, or formulated, for use in many different ways, depending upon the specific active ingredient and the intended use of the product. Non-aqueous liquid formulations have the greatest potential to emit VOC's because of the volatile organic solvents used to prepare the commercial product.

A summary of annual active ingredient (AI) usage and solvent VOC emissions for insecticides and herbicides is presented in

Table 2-1. The basis for these data and all AI usage and solvent VOC emission estimates in this document is the database for insecticides and herbicides developed by Resources for the Future (RFF). Data are presented for total AI usage and emissions from the solvent on a nationwide basis and for only nonattainment areas. Estimations of VOC emissions from insecticides in ozone nonattainment areas were made indirectly based on a proration of herbicide data for VOC emissions nationwide and in nonattainment areas. The total estimated combined VOC emissions due only to nonaqueous solvents from agricultural herbicide and insecticide applications are about 46,400 tons per year on a nationwide basis and about 4,800 tons per year in nonattainment areas. The use of total solvent quantities to estimate VOC emissions assumes complete volatilization of organic solvents, e.g., xylene.

TABLE 2-1. SUMMARY OF ESTIMATED TOTAL AI USAGE AND SOLVENT VOC EMISSIONS FROM INSECTICIDES AND HERBICIDES

	Insecticides <sup>a</sup>	Herbicides <sup>a</sup>	Total <sup>a</sup>
Total nationwide-solvent VOC emissions, tons/yr	3,300	43,100	46,400
Total nonattainment-solvent VOC emissions, tons/yr	800	4,000	4,800
Total nationwide-AI usage tons/yr	43,800	212,000	255,800
Total nonattainment-AI usage tons/yr	10,000	26,000	36,000

<sup>a</sup>All usage data and emissions estimates are based on information in the 1982-1984 and 1987-1989 Resources of the Future (RFF) data bases.

In light of the uncertainties surrounding the fate of the active ingredients, VOC emissions were not estimated for the approximately 256,000 tons of active ingredients applied annually. Active ingredients, except for fumigants, typically have very low vapor pressures. Degradation, adsorption, and absorption compete with volatilization for the fate of the pesticide. Table 4-1 contains a summary of pesticide



volatilization studies. Losses for 16 active ingredients from application and post-application are presented. The California Air Resources Board (CARB) has developed a method for estimating emissions from pesticides. The CARB method, presented in Appendix A, accounts for losses during application, losses from soil or vegetation, and losses to competing mechanisms. Although the CARB method is reasonable, more experimental data are needed to better quantify the VOC emissions from active ingredients in pesticides.

The results of the study indicate that several technically viable methods may apply for reducing VOC emissions resulting from the application of agricultural pesticides. These techniques may be used singly or in combination to achieve the desired level of VOC emission reduction. However, if multiple techniques are suggested, the emission reduction potentially achieved will not be the sum of the individual reduction techniques. Since all the emission reductions were estimated from the baseline condition, after one technique has been implemented, subsequent implementation of additional techniques will have a reduced effect from that discussed in this document. Nonetheless, implementing more than one technique will result in reductions greater than if only one technique were applied. The techniques identified as technically viable for reducing VOC emissions from the application of agricultural pesticides are:

1. Reformulating organic solvent containing pesticide formulations (e.g., emulsifiable concentrates);
2. Reducing fumigant usage;
3. Using alternative application methods;
4. Applying microencapsulation techniques;
5. Using integrated pest management (IPM);
6. Using alternative active ingredients; and
7. Reducing the use of crop oils.

Reformulating existing organic solvent containing pesticides can be an effective technique to eliminate or reduce VOC emissions due to the inert constituents, primarily volatile organic solvents. These solvent-based formulations are widely used

because of low formulation cost and ease of application. A reformulation requirement, implemented over a period of time, would allow time for development and testing of new formulations. The reformulation technique is less costly and time consuming than development of a new active ingredient, which can be a long and costly process for the manufacturer. The annual volatile organic solvent (VOC) contribution to liquid pesticide formulations (e.g., emulsifiable concentrates) is about 93 million pounds (46,400 tons/yr). Of the 46,400 tons/yr, approximately 15,000 tons/yr are found in emulsifiable concentrates and the remainder is present in other organic solvent based liquid formulations. Many manufacturers and formulators of organic solvent based liquid pesticide formulations, in particular emulsifiable concentrates, are attempting to reformulate these products.

Reducing the use of fumigants would lead to a significant decrease in VOC emissions in those States that have a significant usage of field-applied fumigants. In particular, States such as California, Florida, and Texas may benefit from the reduced usage. For many uses, alternative treatment methods or pesticide formulations are available or could be developed. However, if the alternative fumigant is less effective than the compound being replaced, higher application rates may be necessary. This could lead to an increase in VOC emissions. Because a reduction in usage and not an outright ban would occur, the adverse impacts would be considerably lessened on the growers who must use fumigation. Fumigants represent a large emission reduction potential, and a maximum reduction could approximate 41.5 million pounds per year (20,700 tons/yr). This value represents the amount of ethylene dibromide (EDB) and dibromochloropropane (DBCP) used annually as soil fumigants as reported in the RFF data base (1982-1984). Registration for the agricultural use of these two active ingredients has since been cancelled; however, it is assumed that an equal quantity of substitute fumigants, which are also VOC's, has replaced EDB and DBCP. Emission reduction potential for fumigants is discussed in Section 5.2.

Another potential reduction technique is the development and use of alternative improved-efficiency application equipment. One study in California with reduced-volume sprayers indicated a reduction in pesticide application quantities in the 30 to 50 percent range. In addition to the decrease in application quantities, using this equipment may significantly reduce worker exposure and, depending upon the applicator, may reduce drift-related problems.

Microencapsulation is a process whereby very small particles or droplets of the active ingredient are encased by a coating to form very small capsules. Most microcapsules can be envisioned to be small spheres having diameters of a few micrometers to a few millimeters. Using microencapsulation, to the extent it is feasible, could result in a major reduction in VOC emissions from organic solvents in pesticides currently formulated as liquids or emulsifiable concentrates. This technique is not applicable to all active ingredients, but current limitations on this method often are more economic than technical for the manufacturer.

Integrated pest management (IPM) programs use numerous methods to control pests, including pesticides. IPM results in a more effective use of pesticides and, under certain circumstances, may be a mechanism to potentially reduce the overall usage of pesticides. An IPM program is a pest population management system which integrates chemical, biological, and cultural methods into a program to reduce or so manipulate pest populations that these populations are maintained at tolerable levels while providing protection against hazards to humans, domestic animals, and the environment. The IPM program has been used with varying degrees of success for more than 20 years and, in selected instances, can be an effective program. In the optimum situation, IPM can play a significant role in the reduction of pesticide use, overall pesticide exposure to humans, contamination of the environment, and potential impacts on endangered and other species of wildlife.

Two other techniques that could be implemented are the reduced usage of selected active ingredients in formulations and

a reduced usage of crop oils. Both of these techniques require that alternative formulations or the same formulation using lower-VOC-content solvents can be developed or are already available. Use of these techniques could be directed towards selected crops or certain seasons of the year but neither of these techniques are anticipated to be major methods to reduce VOC emissions.

A plan to reduce the total usage of specific pesticide active ingredients could be initiated to target those products for which lower-VOC active ingredient substitutes are readily available or could be developed. This technique may also be employed if the use of the active ingredient at current levels is considered optional or marginal. Careful analyses must be performed to ensure that the alternative active ingredient formulation would not increase VOC emissions due to a significantly higher application rate necessary to achieve the same efficacy as the active ingredient being replaced.

Crop oils are petroleum-based products used as herbicides, carriers for synthetic herbicides, or insecticides. Typically, crop oils are used as insecticides where the application is designed to kill the insects by suffocation but allow the plant to remain unharmed. The use of crop oils has been decreasing in favor of synthetic substitutes that have lower VOC-emitting potential because of lower application rates.

These seven VOC emission reduction techniques have many potential impacts on current pesticide application methods. Implementation of these techniques may result in corresponding increased costs. Some of the techniques are based on an overall reduction in pesticide usage whereas others necessitate a change in the current formulation of the pesticide. Very few cost data were available, but the most significant cost impacts are likely to be Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) registration costs incurred by the manufacturers. With many of the techniques, no change in applicator equipment will be necessary for the consumer. For some techniques, the farmer may need to purchase new or special equipment. The cost impact to

the farmer depends upon the equipment owned by the farmer, size of the farm, type of crops, and the chosen alternative application method.

Please note that three independent data bases are discussed in this report. The National Pesticide Use Inventory compiled by RFF was used for emission and usage estimates in this report. The RFF data base reflects usage of herbicides during 1987-1989 and insecticides during 1982-1984. The 1987 California Pesticide Use Report compiled by the Department of Pesticide Regulation (formerly compiled by the Department of Food and Agriculture) is presented for the reader's information in Appendix A. Data from the 1991 Field Crops Summary published by the U. S. Department of Agriculture were used in Table 3-10, which gives 1991 usage estimates for the top 30 pesticides used on eight crops.

### 3.0 SOURCE CHARACTERIZATION AND PROCESS DESCRIPTION

This section provides a profile of agricultural pesticide use. It discusses the major pesticide categories (Section 3.1), presents information on formulations (Section 3.2) and application processes (Section 3.3), and provides data on pesticides use and trends (Section 3.4).

#### 3.1 PESTICIDES

In most State and Federal laws, pesticides are called economic poisons and are defined as "any substance used for controlling, preventing, destroying, repelling, or mitigating any pest." Pesticides are classified either according to the type of pest they are used against (for example, fungicides kill fungi) or by their mode of action (for example, growth regulators stimulate or retard the growth of plants or insects). Although there are more than 25 pesticide classes, the most widely used pesticides, particularly in agriculture, are herbicides and insecticides.

##### 3.1.1 Herbicides

Herbicides are chemical weed killers that are used extensively on farms and other areas. Herbicides are grouped using a multiple-classification system based on selectivity, mode of action (contact versus translocation), timing of application, and areas covered. Herbicides are classed as selective when they are used to kill weeds without harming the crop and as nonselective when the purpose is to kill all vegetation. Contact herbicides kill the plant parts to which the chemical is applied, whereas translocated (systematic) herbicides are absorbed by roots or above-ground parts of plants and then circulate within the plant system to distant tissues.<sup>1</sup>

Preplant herbicides are applied to an area a few days or weeks before the crop is planted. Preemergent herbicides are applied after planting but before the crop or weed emerges. Postemergent herbicides are applied after the crop or weed emerges from the soil. Banded herbicide applications treat a continuous strip, as along or in a crop row. Broadcast herbicide applications cover an entire area, including the crop. Spot herbicide treatments are made to small areas of weeds. Directed herbicide sprays are applied to selected weeds or to the soil to avoid contact with the crop.

Herbicides are also grouped according to chemical classification. Most herbicides used today are synthetic organic compounds. Although inorganic compounds were, in fact, the first chemicals used to control weeds, they are gradually being replaced by organic compounds. The EPA restricted the use of inorganic compounds because of their persistence in soil.

### 3.1.2 Insecticides

Until the introduction of synthetic organic insecticides in 1940, a variety of materials had been used as insecticides, including extracts of pepper and tobacco, vinegar, turpentine, fish oil, brine, sulfur, hydrogen cyanide gas, and petroleum oils. Since the introduction of synthetic organic insecticides, a variety of compound classes have been used, including organochlorines, organophosphates, organosulfurs, carbamates, formamidines, dinitrophenols, and synthetic pyrethroids.<sup>1</sup> These compound classes have various modes of action including physical toxicants, axonic poisons, central nervous system synaptic poisons, enzyme inhibition, metabolism inhibition, and narcotics.

## 3.2 PESTICIDE FORMULATION

This section presents a brief description of pesticide formulations and overviews of the more common types of formulations.

### 3.2.1 Formulation Process

Developing and manufacturing an active ingredient is only the first step in developing an effective pesticide. A pesticide is rarely used or applied in its pure state; instead, it is first

processed into a more usable form that is applied directly or diluted in the field and then applied. This process is known as formulation. Pesticides are formulated in order to improve their storage, handling, application, effectiveness, and safety properties. The manufacturer of an active ingredient may formulate the final product or sell the active ingredient to a formulator. The formulator may then sell the pesticide under the formulator's brand name or may custom-formulate a product for another firm who sells the product using the firm's brand name.

Many different components may be included in a formulation, depending on the type of formulation and its intended use. In addition to containing a specific concentration of an active ingredient, a formulation may include inert ingredients such as emulsifiers, wetting agents, solvents, thickeners, and anticaking compounds. The right combination of all of these constituents is necessary to ensure an effective final product.

A number of factors are involved in choosing the most appropriate formulation type for an active ingredient. Among these factors are the chemical and physical properties of the active ingredient, including its state (liquid or solid), solubility (oil, water, or neither), melting point, and stability.<sup>1</sup> Other factors considered in selecting a formulation type are packaging requirements, storage and handling problems, worker safety, and method of application. In many cases, one formulation of an active ingredient may be best suited for one purpose, while a different formulation is more appropriate for another application. Several types of formulations might be used, depending on the desired end use of the product, although there are cases in which the chemical and physical properties of the active ingredient preclude all but one formulation type.

### 3.2.2 Types of Formulations

Pesticides are generally classified according to their final form or method of application. Sprays, dusts, aerosols, granules, fumigants, and microencapsulations are common types of formulations. Some of these categories are further divided into more specific subcategories. The advantages and



disadvantages of each formulation type are summarized in Table 3-1. The following subsections present an overview of the most common formulation types.

#### 3.2.2.1 Sprays

3.2.2.1.1 Emulsifiable concentrates. Emulsifiable concentrates are concentrated solutions of active ingredients dissolved in an organic solvent. Candidates for emulsifiable concentrate formulations are water-insoluble, hydrolytically stable active ingredients. An emulsifier, a surface active substance that stabilizes the suspension of small solvent droplets in water, is added to the concentrated solution so that the concentrate will mix readily with water. The concentrated solution is then diluted with water in the field before application. After the concentrate is diluted with water, it should remain suspended for several days. If it does not, a precipitate may form in the spray tank, resulting in clogged nozzles and uneven application. To avoid precipitation, the emulsion should be agitated during application.

The solvent used in an emulsifiable concentrate is usually an aromatic solvent such as xylene. The percentage of active ingredient in the concentrate ranges from 10 to 50.<sup>1</sup> A gallon of concentrate normally contains 4 to 6 pounds of solvent.

Emulsifiable concentrates are common pesticide formulations because many active ingredients are insoluble in water but are soluble in organic solvents. Emulsifiable concentrates penetrate porous material such as soil and plant surfaces better than wettable powders, which improves their efficacy. Because they are liquid, they are easy to pour and measure for mixing in the field. They do have some drawbacks, however. Many of the organic solvents can be harmful to sensitive plants. Because of the toxicity of the solvent and the ability to penetrate porous surfaces, emulsifiable concentrate spills can be hazardous to the operator from potential inhalation and absorption through the skin. The solvents are also a potentially large source of VOC emissions. The movement by manufacturers away from EC's to dry

TABLE 3-1. COMPARISON OF PESTICIDE FORMULATIONS

Formulation	Mixing/loading hazards	Phytotoxicity	Effect on application equipment	Agitation required	Organic solvent used in formulation
Wettable powders	Dust inhalation	Safe	Abrasive	Yes	No
Dry flowables/ water dispersible granules	Fines inhalation	Safe	Abrasive	Yes	No
Soluble powders	Dust inhalation	Usually safe	Nonabrasive	No	No
Emulsifiable concentrates	Spills and splashes	Maybe	May affect rubber pump parts	Yes	Yes
Flowables	Spills and splashes	Maybe	May affect rubber parts; also abrasive	Yes	Sometimes
Solutions	Spills and splashes	Safe	Nonabrasive	No	Sometimes
Dusts	Severe inhalation hazards	Safe	---	Yes	No
Granules	Fines inhalation	Safe	---	No	No
Microencapsulated	Spills and splashes	Safe	---	Yes	No
Organic solvent based liquids	Spills and splashes	Maybe	May affect rubber pump parts	Yes	Yes

flowables is also driven by the desire to eliminate the container disposal problems for plastic and steel.

3.2.2.1.2 Wettable powders. Wettable powders are concentrated dusts formulated with a finely ground dry carrier (usually mineral clay) and a wetting agent. The wetting agent enhances the ability of the powder to suspend and mix in water. Wettable powders are relatively easy to formulate, are compatible with other pesticides and fertilizers, and tend to be less phytotoxic than other formulations because the carriers are inert materials. However, they do have disadvantages. They require agitation during application, the inert carrier is abrasive and contributes to equipment wear, and dust inhalation by the applicator is a potential problem during handling and mixing. The fine dust particles normally contain a high concentration of pesticide and can remain suspended in the atmosphere for hours. To alleviate some of the handling and mixing problems associated with wettable powders, some manufacturers are packaging wettable powders in water-soluble bags that can be dropped unopened into the filled spray tank.

3.2.2.1.3 Water-soluble powders. Water-soluble powders are relatively simple formulations. The active ingredient is a finely ground water-soluble solid that is mixed with other formulation ingredients to form the water-soluble powder. For application, the powder is added to the spray tank, where it quickly dissolves. Because these formulations form true solutions, they do not require constant agitation in the spray tank and are not abrasive to the equipment. Because of their dusty nature, however, these formulations are potential inhalation hazards to applicators. As with wettable powders, manufacturers are beginning to package soluble powders in water-soluble packages. Although water-soluble powder formulations have many advantages, they are not common because few pesticide active ingredients are soluble in water.

3.2.2.1.4 Flowables. A flowable is a pesticide formulation consisting of a finely ground active ingredient mixed with a liquid carrier and emulsifiers. This type of formulation is used for solid active ingredients that cannot be dissolved in water or other solvents. They have properties common to both emulsifiable concentrates and wettable powders. They require continued agitation to keep them in suspension, and they can cause abrasive wear to equipment.

3.2.2.1.5 Dry flowables. Dry flowable formulations, also known as water-dispersible granules, are small granules containing an active ingredient and emulsifier. The granules are mixed with water prior to application. Dry flowables require little carrier, so they have a high percentage of active ingredient per unit of weight. Another advantage is the elimination of dust problems associated with wettable powders. Because the granules are packaged in easy-to-pour containers, they are easy to measure and mix. Like liquids, they are measured out by volume rather than weight. However, they must be agitated during application and they can be abrasive to application equipment.

3.2.2.1.6 Ultralow-volume concentrates. Ultralow-volume (ULV) concentrates are highly concentrated pesticide solutions, usually containing between 80 and 100 percent active ingredient.<sup>1</sup> If the active ingredient is a liquid, it is generally used without dilution; if it is a solid, it is dissolved in a minimum of solvent, usually vegetable oil. These formulations require application equipment designed to apply a small quantity of extremely fine spray over a large area. They are applied at rates ranging from 0.5 pint to 2.0 gallons per acre, whereas conventional formulations are normally applied at rates ranging from 5 to 20 gallons per acre.<sup>1</sup> They are most effective when applied aerially, because aerial applications can distribute small volumes over land areas more efficiently than can ground applications. However, new ground application techniques such as electrostatic air-atomization sprayers, are being developed to apply ULV concentrates.<sup>2</sup> When using ULV formulations, the

application equipment must be carefully calibrated because of the low volume and high concentration of the active ingredient. Due to the potential toxic effects of such highly concentrated formulations, ULV concentrates are available only for commercial use.

3.2.2.1.7 Water-soluble concentrates or solutions. Liquid pesticides that dissolve in water are called water-soluble concentrates, or solutions. Solution formulations have the advantage of requiring no further mixing or agitation once the pesticide is dissolved. However, like water-soluble powders, the number of water-soluble concentrates is limited by the availability of water-soluble active ingredients.

3.2.2.2 Dusts. Dust formulations consist of a finely ground active ingredient combined with an inert carrier, usually clay. They are easy to formulate and apply. Dusts are usually formulated to contain 1 to 10 percent active ingredient.<sup>1</sup> Dusts are particularly useful when the moisture from a liquid spray may damage the crop or foliage. Despite the advantages of dusts, they are used less frequently than spray applications and their use is continuing to decline. The biggest disadvantage of dusts is the drift hazard associated with their use and their increased cost. In an aerial application of a dust formulation, as much as 90 percent of the pesticide may be lost due to drift.<sup>1</sup> Even the portion that reaches the crop may not deposit and stick on the foliage unless the crop's surface is wet. Dusts can present serious inhalation hazards to applicators if they do not use the proper respiratory protection equipment.

3.2.2.3 Granules. Granules consist of an active ingredient and carrier combined with a binding agent. The carrier, usually clay, is formed into pellets, and the pellets are sprayed with a solution of the active ingredient. The resulting product ranges in size from 20 to 80 mesh, which makes granules much less susceptible to drift than dusts.<sup>1</sup> Granular formulations generally contain from 2 to 25 percent active ingredient.<sup>1</sup> Granules are applied to soils to control weeds, nematodes, and soil insects. They are often soil-incorporated after

application. Foliar applications of granular formulations are not as common as soil applications because the granules bounce off the leaves. However, they can be used on plants like corn because the granules lodge in the leaf whorls. The active ingredient in a granular formulation is usually released slowly as the granule dissolves. This slow release is often an advantage in terms of product efficacy, but it is potentially hazardous to wildlife that eat the slow-dissolving granules.

3.2.2.4 Fumigants. Fumigants are volatile compounds used to treat (1) pests in stored products; (2) soil pests such as insects, nematodes, and micro-organisms; and (3) some weeds. They are also used to control pests in ships, aircraft, residences, warehouses, greenhouses, and commercial buildings.<sup>1</sup> Fumigants may be solid, liquid, or gaseous. Solid and liquid fumigants volatilize during or immediately after application. Fumigants present a serious inhalation hazard to applicators and others in or near the treated area. Applicators should use respiratory protection equipment and wear protective clothing. Soil fumigants are usually applied through an irrigation system or injected into the soil. In many cases, the soil is covered with plastic sheets for several days in order to retain the volatile chemical and maintain an effective concentration. Several factors influence the effectiveness of a soil fumigant, including soil type, soil organic matter concentration, soil temperature, and weather conditions during and after application.<sup>1</sup>

3.2.2.5 Microencapsulated Pesticides. Microencapsulated formulations consist of liquid or solid pesticide enclosed in small plastic capsules. The microcapsules are then mixed with water and sprayed on the target. During the spray application, some drift may occur. After spraying, the active ingredient is slowly released as the plastic coating degrades. The quantity of VOC solvent contained in the microcapsule will be exposed to the environment but at a much slower rate than for non-aqueous liquid formulations (e.g., emulsifiable concentrates). Although microencapsulated pesticides are not widely used, they have many

advantages. Because the active ingredient is covered with a coating, applicators do not have any contact with the active ingredient and there is no odor. The slow-release mechanism prolongs the effectiveness of the pesticide, which allows for fewer and less precisely timed applications. The pesticide also volatilizes more slowly, so post-application drift is minimal.

### 3.3 PESTICIDE APPLICATION

Pesticides may be applied as liquids, dry solids, or gases. Liquid pesticides are applied as a spray of water or oil droplets containing a solution or suspension of active ingredient. Pesticides formulated as dusts or granules are normally applied dry. Pesticides that exist in a gaseous state at ambient temperature and pressure may be applied either as gases or pressurized liquids or as solids that vaporize upon release. This type of pesticide application is known as fumigation.

For all types of pesticide applications, the ultimate goal is to develop an understanding of the factors that affect application efficiency and how it can be improved.<sup>3</sup> Application efficiency is defined as follows:

$$\text{Application efficiency, \%} = \frac{\text{Minimum pesticide volume required}}{\text{Actual pesticide volume applied}} \times 100$$

Few figures on the application efficiency of field spraying operations are available, and those that are quoted vary widely from <1 percent to 60 percent.<sup>3</sup> If most farm spraying operations are considered to have a spraying efficiency of only 5 to 10 percent, at best, the scope for improvement in efficiency from better equipment and application practices can be significant.<sup>3</sup> Improvements in spray efficiency are one means of reducing VOC emissions from the application of pesticides.

Application efficiency can be improved in several ways. The State agricultural extension service could make available information on the basic principles of pesticide application and, if needed, assist the farmer in applying these principals.

Applying a liquid pesticide requires a knowledge of how spray droplets are produced, how they are transported to the target, and how they deposit and adhere to different types of targets. Applying a granular pesticide requires a knowledge of soil conditions that are most conducive to a high level of product efficiency. Efficient fumigation requires that the applicator be aware of the properties of the fumigant and its mode of action and of soil conditions that have a major influence on fumigation effectiveness. The applicator also needs to be familiar with all of the equipment options available and what type of equipment can most effectively deliver a particular product in a particular situation. All measuring, mixing, and application equipment must be well maintained and calibrated to ensure that the right amount of product is delivered to the target. Application efficiency can also be improved by minimizing drift, which reduces the amount of pesticide reaching the target. In addition to reducing application efficiency, drift can also endanger neighboring crops, livestock, wildlife, and humans, as well as general environmental contamination.

### 3.3.1 Liquid Pesticide Application

3.3.1.1 Principles of Application. Producing and delivering to the target optimum-sized spray droplets is probably the most important aspect of liquid pesticide application. Most conventional liquid sprayers produce a wide range of droplet sizes, averaging from 40 to 500 microns ( $\mu\text{m}$ ) in diameter.<sup>3</sup> Droplets at the lower end of this range, 40 to 100  $\mu\text{m}$ , generally provide better target coverage, which is particularly important when applying an insecticide or fungicide to foliage.<sup>3</sup> However, these droplets are also extremely susceptible to drift. Larger droplets, 400 to 500  $\mu\text{m}$ , are much less susceptible to drift because they are heavier and fall quickly, but they are less effective for some types of pest control because they may bounce or run off target surfaces and not provide adequate coverage for pest control.<sup>3</sup> The goal in liquid pesticide application is to generate droplets that are small enough to provide adequate target coverage but large enough to minimize spray drift. For



most pesticide applications, the optimum range for droplets is 100 to 300  $\mu\text{m}$ .<sup>3</sup>

3.3.1.2 Application Equipment. A list and brief description of liquid pesticide application equipment is included in Table 3-2. Liquid pesticide application equipment ranges from small aerosol cans to air blast sprayers with tank capacities of up to 1,000 gallons capable of spraying up to 1,000 gallons per acre. Of the application methods listed, controlled droplet applicators, ultralow volume applicators, and electrostatic sprayers have the greatest potential for increasing application efficiency.

In terms of application efficiency, wick applicators are probably the best type of pesticide application available. Their basic design consists of a cloth, rope, or wick saturated with herbicide, which is wiped onto the leaves of target weeds. Because these applicators apply the herbicide directly to the weed, there is little if any pesticide wasted, and application efficiency approaches 100 percent. Unfortunately, wick applicators are limited to the application of systemic or contact herbicides in situations where the weeds are taller than the crop.

Controlled droplet applicators (CDA's) produce droplets ranging in size from 100 to 400  $\mu\text{m}$ .<sup>3</sup> By limiting the size range, these applications eliminate the production of small droplets that are subject to drift and large droplets that may bounce or roll off the target. Controlled droplet applicators may be used in a variety of ways. Some are self-contained, hand-held units, while others are connected to a backpack tank by a flexible hose. One or more controlled droplet applicators can be mounted to a boom and attached to a tractor. They may also be used in place of nozzles in air blast sprayers. Controlled droplet applicators are most often used to apply herbicides, but they can also be used for some insecticide and fungicide applications. They are particularly useful in very-low-volume application because by applying uniform sized droplets they minimize the drift generally associated with these types of applications.

TABLE 3-2. LIQUID PESTICIDE APPLICATION EQUIPMENT

Type	Uses	Suitable formulations	Comments
Powered backpack sprayer	Aquatic, landscape, right-of-way, forest, and agricultural applications.	All. Some may require agitation.	Requires frequent maintenance.
Controlled droplet applicators	Contact herbicides and insecticides.	Usually water-soluble formulations.	Fragile.
Low-pressure sprayers	Common commercial sprayer for multiple pest control.	All. May include agitator.	Requires frequent maintenance.
High-pressure hydraulic sprayer	Landscape, right-of-way, and agricultural. Dense foliage and large trees.	All. May include agitator.	Requires frequent maintenance. Pumps and nozzles subject to rapid wear.
Air blast sprayer	Applications to trees, vines, and shrubs	All. Usually equipped with agitator.	Requires frequent maintenance.
Ultralow-volume applicators	Agricultural and aquatic applications.	Usually only pesticides soluble in organic solvents.	Requires extreme care in calibration.
Electrostatic sprayers	Agricultural applications to trees, vines, and row crops.	All. Some may require agitation.	Usually equipped with blower.

Ultralow-volume sprayers apply from 0.5 pint to 2 gallons of highly concentrated spray per acre.<sup>1</sup> Low-volume nozzles or controlled droplet applications are used to break up the spray into small droplets that are propelled to the target by air from a fan or blower. Because ULV sprayers normally apply very small droplets that are subject to rapid evaporation, the pesticide is sometimes mixed with vegetable oil carriers, which reduce the droplet evaporation rate. They are also usually limited to application during low winds to minimize drift. It is extremely important that ULV sprayers be calibrated accurately because of the high concentration of pesticide being applied.

Electrostatic sprayers apply small, electrically charged pesticide droplets. Droplets average about 50  $\mu\text{m}$  in diameter and are given a negative electrostatic charge as they leave the sprayer. In theory, plant material has a positive electrostatic charge and the droplets are attracted to the surface thereby increasing pesticide deposition and target coverage. Not all experimental studies support this theory. A study by Law and Cooper on orchard air carrier sprayers showed that while significant deposition increases could be achieved by electrically charging the more finely divided droplets, the deposition was not increased to the level achieved by the larger droplets produced by hydraulic nozzle in conventional orchard sprayers.<sup>4</sup> However, one of the study conclusions was that the highly significant deposition controls achieved by charging finely divided droplets shows that an electrostatic benefit can be obtained in applications to orchard air carriers. These results may initiate engineering design changes (e.g., increased droplet charge level) leading to improvements in deposition that could surpass levels currently achieved during treatment with conventional large volume median diameter droplets.

### 3.3.2 Dry Pesticide Application

3.3.2.1 Principles of Dust Application. The application of pesticides as dust formulations has declined considerably because of operator safety and low application efficiency. Dusts are extremely susceptible to drift. Particles that do reach the

target often do not adhere to the target surface. Drift can be minimized by limiting applications to days of favorable weather conditions. Adhesion to the target can also be improved by formulating the product with adhesives or stickers. However, even under the most favorable conditions, dust application efficiency is very low.

3.3.2.2 Principles of Granule Application. The application efficiency for granular applications is most affected by soil conditions. Because most granule formulations are designed to release active ingredient through leaching by soil water, they are most effective when applied to wet soil.<sup>3</sup> Ideally, the soil should be irrigated both before and after the granules are applied and incorporated. Higher soil temperatures may also increase the effectiveness by enhancing the release of the active ingredient.

3.3.2.3 Dust and Granule Application Equipment. A list and brief description of the equipment used to apply dusts and granules is included in Table 3-3. Except for the bulb applicators, which are normally only used for small indoor jobs, all of the dust applicators present a considerable drift hazard.<sup>5</sup> Because granules have a much lower drift potential than either liquids or dusts, all of the granule applicators are fairly efficient, although the mechanically driven granule applicator requires extra attention to ensure it is accurately calibrated. In general, differences among granule applicators are a difference in scale, not in application efficiency.

### 3.3.3 Fumigation

Soil fumigants are applied in the following ways:

1. Injected into the soil as a liquid;
2. Applied in a granular form and incorporated by cultivation; and
3. Released in a gaseous state above the soil surface but beneath a sealed plastic cover. As with granule applications, soil conditions are most influential in determining fumigation effectiveness. The soil must be neither too wet nor too dry when applying a fumigant. Wet soils trap the fumigant in soil water,

TABLE 3-3. DUST AND GRANULE APPLICATION EQUIPMENT

Type	Uses	Suitable formulations	Comments
Dust applicators			
Bulb applicator	Applies dusts to small cracks and crevices.	Dusts	Easy to use.
Compressed air duster	Applies dust in confined spaces, e.g., wall voids.	Dusts	Inhalation hazard.
Mechanical duster	Landscape and small agricultural uses.	Dusts	Drift hazard, inhalation hazard.
Power duster	Vine crops. Also used in buildings.	Dusts	Drift hazard.
Granule applicators			
Hand-operated applicator	Landscape, aquatic and some agricultural areas.	Granules or pellets	Easy to use.
Mechanically driven applicator	Turf, landscape and some agricultural areas.	Granules or pellets	Requires accurate calibration.
Powered granule applicator	Agricultural areas--usually row crops.	Granules or pellets	Requires frequent maintenance.

slowing down or preventing fumigant movement through the soil. In soils that are too dry, the gas may diffuse so rapidly that it is not retained long enough to be lethal to the target organism. Fumigation effectiveness is also improved by higher soil temperatures. Higher temperatures enhance vaporization and diffusion of the fumigant in the soil, decreasing the concentration and time required for a lethal dose. In addition, some soil pests (e.g., nematodes) are more susceptible to fumigants at higher soil temperatures.

#### 3.3.4 Aerial Pesticide Application

Both liquid and dry pesticide formulations are applied aerially. Liquids are usually applied from boom configurations attached to the plane's wings. Aerial application efficiency can be improved by proper nozzle placement, avoiding unfavorable weather conditions, and using viscosity additives.<sup>3</sup> Granules can be applied aerially, but they must be heavy enough to reach the target without being affected by wind drift. Aerial dust applications are not recommended because dust particles are too small to reach the target area.

#### 3.3.5 Maintenance and Calibration

Effective pesticide application depends on properly maintained and calibrated application equipment. A periodic maintenance program can prevent accidents or spills caused by ruptured hoses, faulty fittings, damaged tanks, or other problems.<sup>5</sup> Because operators often fail to understand how quickly equipment becomes maladjusted and worn, most sprayers are not calibrated often enough. The main reason for calibrating pesticide application equipment is to determine how much pesticide must be put into the spray tank to ensure that the correct amount of chemical is applied. Failure to calibrate equipment properly is a frequent cause of ineffective pesticide applications and overuse of pesticides.

#### 3.3.6 Minimizing Drift

Pesticide drift is movement of a pesticide away from the treatment site. There are several factors that influence drift and a number of ways to reduce it: less volatile active

ingredients can be used and thickeners can be added that reduce pesticide evaporation potential by increasing liquid viscosity to the spray tank. Thickeners do not act to reduce the total emissions but rather to increase viscosity to minimize drift problems.

Controlling spray droplet size may be the most important factor in reducing drift. Small droplets, in particular those less than 100  $\mu$ m, are more vulnerable to both spray droplet drift and vapor drift. Small droplets are more likely to drift away from the target zone and to evaporate. Using larger nozzles and lowering the output pressure of a sprayer reduces the production of small droplets. Controlled droplet applicators generate droplets ranging in size from 100 to 400  $\mu$ m, eliminating the very small droplets most susceptible to drift.<sup>5</sup> Overall, drift reduction procedures only work if the applicators actually reduce the usage rate of the formulation to account for improved efficiency.

#### 3.3.7 Pesticide Application: Sources of VOC Emissions

Volatile organic compounds may be emitted via one or several potential pathways. Emissions due to volatile active ingredients and the organic solvents used in the formulations may be two major sources of VOC's following field application of the pesticide. Evaporation of volatile components in a pesticide spray before it reaches the target or entrainment of the pesticide as an aerosol may also contribute to VOC emissions.

During field application and subsequent to the application, several factors influence the extent and rate of VOC emissions such as target soil, type of vegetation, type of spray equipment, physical and chemical properties of the active ingredient and solvent, the type of surface to which the pesticide is applied, and the extent of post-application incorporation.

Following field application, the fate of a pesticide, be it xenobiotic or natural, is governed by several factors including loss from soil surface, hydrolysis, biodegradation route and rate, diffusion processes, sorption, mobility, binding, and biological persistence. Superimposed on these factors,

characteristics in three other areas also impact the fate of the pesticide: (1) chemical structure of the pesticide, (2) soil properties, and (3) climatic conditions. Chemical structure includes reactivity, vapor pressure, photolytic stability, adsorptive properties, and biological properties. Soil properties include organic content, water content, soil texture, pH, microbial availability, and water flow. Climatic conditions include factors such as temperature, amount of sunlight, rainfall, and evaporation rate. Fate is determined by the complex interactions of all three of these areas. The key processes by which the fate of the pesticide is defined are generally recognized to be adsorption by the soil, volatilization of the pesticide from the soil, and the rate of degradation by biotic and abiotic processes.<sup>6</sup> Several of the factors impacting the fate of pesticides are briefly discussed in the following subsections.

3.3.7.1 Vapor Pressure. One of the major physical properties that governs the emission of a compound into the environment is the vapor pressure. A pesticide formulation is generally composed of a variety of constituents and each constituent has a specific function in the product. Each constituent has a characteristic vapor pressure that will dictate, in part, the emission of that constituent into the environment and the range of the vapor pressures found in a pesticide formulation can be very wide. Table 3-4 presents vapor pressure data for selected active ingredients, fumigants, and selected solvents commonly found in pesticide formulations. In general, the nonfumigant active ingredients exhibit vapor pressures that range from  $10^{-4}$  to  $10^{-7}$  mm Hg at ambient temperatures. These vapor pressures are two to three orders of magnitude less than either fumigants or the solvents. Because of their mode of action, it is necessary for fumigants to have a relatively high vapor pressure compared to other pesticide active ingredients. If the potential for volatilization from a pesticide formulation, particularly an EC, was based solely on the vapor pressures of the active ingredients, an incorrect



TABLE 3-4. VAPOR PRESSURE DATA FOR SELECTED  
PESTICIDE FORMULATION COMPONENTS

Component	Phys. state	Vapor pressure (mm Hg) @20-25°C
<b>ACTIVE INGREDIENTS</b>		
<b>1. Insecticides; including miticides, larvicides, nematicides, and acaricides</b>		
Chlorpyrifos	solid	$1.7 \times 10^{-5}$
Terbufos	liquid	$3.2 \times 10^{-4}$
Fonophos	liquid	$3.4 \times 10^{-4}$
Carbofuran	solid	$6 \times 10^{-7}$
Phorate	liquid	$6.4 \times 10^{-4}$
Methyl parathion	solid	$1.5 \times 10^{-5}$
Aldicarb	solid	$3 \times 10^{-5}$
Acephate	solid	$1.7 \times 10^{-6}$
Dicrotophos	liquid	$1.6 \times 10^{-4}$
Dicofol	liquid	$4.0 \times 10^{-7}$
Ethoprop	liquid	$3.8 \times 10^{-4}$
Diazinon	liquid	$6 \times 10^{-5}$
Dimethoate	solid	$2.5 \times 10^{-5}$
Permethrin	solid	$1.3 \times 10^{-8}$
Propargite	liquid	$3 \times 10^{-3}$
Trimethacarb	solid	$5.1 \times 10^{-5}$
Azinphos-methyl	solid	$2 \times 10^{-7}$
Ethyl parathion	liquid	$5 \times 10^{-6}$
Methomyl	solid	$5 \times 10^{-5}$
Oxamyl	solid	$2.3 \times 10^{-4}$
Profenofos	liquid	$9 \times 10^{-7}$
Thiodicarb	solid	$1 \times 10^{-7}$
Disulfoton	liquid	$1.5 \times 10^{-4}$
Fenamiphos	solid	$9.8 \times 10^{-7}$
Endosulfan	solid	$1.7 \times 10^{-7}$
Methamidophos	solid	$8 \times 10^{-4}$
<b>2. Herbicides</b>		
Atrazine	solid	$2.9 \times 10^{-7}$
Alachlor	solid	$1.4 \times 10^{-5}$

TABLE 3-4. (continued)

Component	Phys. state	Vapor pressure (mm Hg) @20-25°C
Metolachlor	liquid	$3.1 \times 10^{-5}$
Cyanazine	solid	$1.6 \times 10^{-9}$
Trifluralin	solid	$1.1 \times 10^{-4}$
EPTC	liquid	$3.4 \times 10^{-2}$
Pendimethalin	solid	$9.4 \times 10^{-6}$
Butylate	liquid	$1.3 \times 10^{-2}$
Propanil	liquid	$4 \times 10^{-5}$
2,4-D acid	solid	$8 \times 10^{-6}$
Metribuzin	solid	$<1 \times 10^{-5}$
Molinate	liquid	$5.6 \times 10^{-3}$
Propachlor	solid	$2.3 \times 10^{-4}$
Fluometuron	solid	$9.4 \times 10^{-7}$
Clomazone	liquid	$1.4 \times 10^{-4}$
MCPA	solid	$1.5 \times 10^{-6}$
Bromoxynil (octanoate)	solid	$4.8 \times 10^{-6}$
Prometryn	solid	$1.2 \times 10^{-6}$
Ethalfuralin	solid	$8.8 \times 10^{-5}$
Norflurazon	solid	$2 \times 10^{-8}$
EPTC	liquid	$3.4 \times 10^{-2}$
Linuron	solid	$1.7 \times 10^{-5}$
Simazine	solid	$2.2 \times 10^{-8}$
3. Fumigants, fungicides, and others		
Chloropicrin	liquid	18
1,3-Dichloropropene	liquid	29
Methyl bromide	gas	1,824
Chlorothalonil	solid	$5.7 \times 10^{-7}$
Tribufos	liquid	$1.6 \times 10^{-6}$
Ethephon	solid	$<10^{-7}$
PCNB	solid	$1.1 \times 10^{-4}$
Benomyl	solid	$<1 \times 10^{-10}$
Metam-sodium	solid	20 <sup>a</sup>
Dimethipin	solid	$3.8 \times 10^{-9}$

TABLE 3-4. (continued)

Component	Phys. state	Vapor pressure (mm Hg) @20-25°C	
Thidiazuron	solid	2.3 x 10 <sup>-11</sup>	
SOLVENTS			
Chlorobenzene (mono)	liquid	10	22°C
Ethylbenzene	liquid	10	26°C
Trimethylbenzene (1,2,4)	liquid	1 (est.)	20°C
Water	liquid	17.5	20°C
m-Xylene	liquid	10	28°C
Xylene-mixtures	liquid	7	25°C

<sup>a</sup>Value for major residue: methyl isothiocyanate

Sources:

1. Farm Chemical Handbook 1992. Meister Publications Company, Willoughby, Ohio.
2. Handbook of Chemistry and Physics, 67th Edition (1986-1987). CRC Press, Boca Raton, FL. 1987.
3. Wauchope, R.D., T.M. Buttler, A.G. Hornsby, P.W.M. Augustijn-Beckers, and J.P. Burt. The SCS/ARS/CES Pesticide Properties Database for Environmental Decision-Making. In: Reviews of Environmental Contamination and Toxicology, G.W. Ware, Editor. Volume 23. Springer-Verlag, New York. 1992.

conclusion could be drawn that pesticides are basically nonvolatile and that evaporation during and subsequent to field application is limited. However, the most significant reductions in emissions of volatile compounds results from reducing the solvent content of the formulation and generally not from reducing the quantity of active ingredient.

After application of the pesticide, several mechanisms can affect the degree of emissions of the volatile components. The vapor pressure of the components is a major factor in determining those emissions. As evidenced in Table 3-4, the solvents have significantly higher vapor pressures than the nonfumigant active ingredients. For formulations having a high solvent content, the solvent would volatilize and leave the active ingredient (and other nonvolatile components) on the soil or plant surface. On the soil or plant surface, the active ingredient may be taken up by the plant, volatilize, be transported to the soil surface by rain, or undergo degradative reactions on the surface.

3.3.7.2 Soil Moisture Content. For pesticides applied to soils, the soil moisture content is one of the most important factors affecting the rate of volatilization. Pesticides applied to dry soils do not volatilize as rapidly as pesticides applied to moist soils. As the soil is moistened, the rate of volatilization increases.

A number of researchers have investigated the effect of soil moisture on pesticide volatilization.<sup>7,8</sup> Results from these studies showed much smaller vapor losses for pesticides applied to air dry soils than for pesticides applied to soils moistened to field capacity. The same pattern of results were obtained with soil types varying from sand to silty clay loam.

The inhibited volatilization of pesticides applied to dry soil surfaces is believed to be due to increased adsorption of the pesticide on dry soil. At and above a particular moisture level there is a monomolecular water layer on the soil surface. When the moisture content drops below this level, adsorption sites are exposed. Pesticide molecules can then bond to these exposed sites, thus reducing their fugacity (escaping tendency)

and vapor density. If the soil is remoistened, the water molecules will displace the pesticide accumulated at the surface adsorption sites and the pesticide will evaporate.

Soil moisture content is also an important factor in determining the extent of volatilization of pesticides that have penetrated beneath the soil surface or have been mixed into the soil. Three factors affect the volatilization of pesticides that are beneath the soil surface: desorption of the pesticide from the soil, upward movement of the pesticide to the soil surface, and vaporization into the atmosphere. The upward movement of the pesticide to the soil surface is affected by the moisture content of the soil. As water evaporates from the soil surface, it creates a concentration gradient, which causes water in the soil to move upward toward the surface to replace the evaporated water. Pesticides in the solution will move to the surface with the water. At the soil surface, the pesticide is available for evaporation. This concurrent movement of pesticides to the surface with the water has been called the "wick effect."<sup>9</sup> In dry soils, the water evaporation rate is low, so the movement of pesticides to the surface is limited. For moist soils, the water evaporation rate is higher and the pesticide moves more quickly to the surface, where it may evaporate into the atmosphere.<sup>10</sup>

3.3.7.3 Pesticide Incorporation Into Soil. Some pesticides, particularly preemergent herbicides, are incorporated into the soil immediately after application; that is, they are mechanically mixed into the soil by disking or tilling. The pesticide may be incorporated by disking to shallow depths in soils (2.5 cm), or it may be incorporated to greater depths (7.5 cm) by tilling. For some pesticides, incorporation increases the efficacy; for others, incorporation is required for safety reasons. For incorporated pesticides the rate of volatilization is controlled primarily by pesticide movement through the soil to the surface.

Two factors are particularly important in limiting the volatilization of incorporated pesticides. First, the soil concentration of an incorporated pesticide may be as much as an

order of magnitude less than the soil concentration of a surface-applied pesticide because it is mixed into the soil at depths of 2 to 8 cm as opposed to the 3 to 5 mm depth to which formulation spray drops generally penetrate. The lower concentration decreases the pesticide equilibrium vapor pressure, thus reducing the volatilization rate. Second, because the pesticide is incorporated to a greater depth, it will have a greater distance to travel before it reaches the surface and will encounter greater upward movement resistance.<sup>9</sup>

3.3.7.4 Application to Foliage. When a pesticide is applied to vegetated land, part of the total amount applied is retained by the crop foliage, while some portion is deposited on the underlying soil. The percentages which are deposited on soil and on foliage are dependent upon several factors, including crop type, extent of foliage coverage, and application method. Field studies evaluating the volatilization of pesticides applied to vegetated surfaces have utilized this partitioning of the total deposit to compare volatilization rates for pesticides from soil and foliage. While volatilization has been shown to be a major source of pesticide loss from foliage, photolytic degradation, hydrolysis of the AI, and other degradation mechanisms may be factors in pesticide loss.

Studies have demonstrated that the rate of volatilization from vegetation is rapid for the first day, gradually decreases for the next week, and then drops off significantly. Results from field studies demonstrate that volatilization from plant surfaces is much more rapid than volatilization from soil surfaces for the first few days following the application.<sup>11</sup>

The gradual decrease in the rate of pesticide volatilization that is observed during the first week is proportional to the amount of remaining residue. When the pesticide is first applied, the leaf surface is covered by a layer of pesticide residue. When this layer quickly volatilizes, islands of residues are formed. As these islands decrease in size, the volatilization rate per unit of leaf area also decreases.

Two theories have been proposed for the further decrease in volatilization after the first week. The first theory suggests that residues entrapped in leaf surface irregularities are the last to volatilize. These residues have less exposed surface area than the islands of residues, so that the rate of loss is no longer proportional to the amount of residue remaining. The other theory suggests that the last residues to evaporate are those that have penetrated the leaf surface and become adsorbed on intercellular material. This adsorption of the pesticide reduces its equilibrium vapor pressure, thus reducing its volatilization rate. Both mechanisms are probably partially responsible for the observed reduction in evaporation rate.<sup>11</sup>

3.3.7.5 Pesticide Loss by Sorption. Adsorption and absorption rates for pesticides vary depending on the chemical nature of the pesticide, meteorological conditions, and the application site. Most sorption processes are reversible. For the majority of pesticides only a small percentage is irreversibly adsorbed and unavailable for evaporation. Because of the variables involved, it is impossible to determine a value for sorption loss for every pesticide application. However, a VOC emissions methodology developed by Eureka Laboratories for the California Air Resources Board (CARB) recognized that some portion of quantity pesticide applied per acre is unavailable for evaporation due to sorption over a considerable or indefinite time period. It was therefore assumed sorption losses to be 2 percent of the amount of the pesticide applied per month.<sup>12</sup>

3.3.7.6 Pesticide Loss by Degradation. Pesticides are degraded in the environment by a number of mechanisms, including chemical, photochemical, and biological degradation. Although most pesticides are susceptible to one or more of these degradation mechanisms, the quantity of hydrocarbon compounds available for vaporization and atmospheric reaction is not necessarily reduced. A pesticide may be split into two smaller compounds by degradation mechanisms, but this does not change the total mass available for evaporation.

Although there is no established procedure or model for predicting degradation losses for pesticides, it is apparent that some portion of most pesticides is unavailable for evaporation due to degradation processes. The CARB method to estimate emissions from pesticide application assumed that 4 percent per month is lost and unavailable for evaporation.<sup>12</sup>

There are, however, many possible fates and losses of pesticides in the environment not considered in CARB's calculations. Drift and evaporation occur during application. Pesticides also volatilize from soil and vegetation surfaces. Atmospheric precipitation runoff transports pesticides to aquatic ecosystems. Pesticides adsorb to soils and may be transported by erosion. Chemical, photochemical, and hydrolytic degradation of the pesticide and its decomposition products occurs. Pesticides are also degraded biologically or may bioaccumulate in various organisms. Which of these several degradation mechanisms and transport pathways occurs depends on the chemical and physical properties of the pesticide and environmental conditions.

The rates of the various degradation processes vary widely both within the type of process and between types of processes. For example, the hydrolytic halftimes for some selected AI's are as follows: chlordane ( $1.8 \times 10^5$  yr), lindane (182 d), methoxychlor (365 d), heptachlor (4 to 5 d), captan (3 hr), atrazine (2 to 3 hr), and chlorothalonil (38 d @ pH 9).<sup>13,14,15</sup> Heptachlor and captan are no longer registered for use in the U.S. Chlordane and lindane are "restricted use pesticides." Soil degradation rates for selected AI's are: methomyl (3 to 5 d), metolachlor (over 64 d), acephate (3 to 6 d), and bentazon, Na salt (4 mo).<sup>15</sup> Acifluorfen, Na salt has a reported photodegradation halftime of 4.5 days.<sup>15</sup>

#### 3.4 PESTICIDE USE AND TRENDS IN THE UNITED STATES

World usage of pesticides is valued at approximately \$23 billion annually. The United States is the leading user of pesticides, accounting for an estimated 29 percent of the total world volume of pesticide usage (in pounds of active ingredient) in 1989. The United States produced approximately 1.3 billion



pounds [lb] of the active ingredients used in pesticides, valued at \$7.5 billion retail.<sup>16</sup>

In the United States, 120 firms manufacture the active ingredients used in pesticides. The leading six companies represent 65 percent of production.<sup>17</sup> Active ingredients must be prepared in suitable solutions and forms before they can be applied to fields. This is accomplished by 3,000 formulators in the nation, responsible for more than 21,000 registered products.<sup>16</sup> The agricultural market is the leading sector for pesticide use in the United States and accounts for 75 percent of the total usage. Industrial and government use follows with 18 percent of total pesticide use, while home and garden use accounts for 7 percent.<sup>16</sup>

#### 3.4.1 Pesticide Use in the United States

Figure 3-1 shows the total agricultural share of pesticide use (in million pounds of active ingredient), based on EPA estimates, in the United States from 1964 to 1989.<sup>18</sup> The figure shows a fairly rapid growth in pesticide use from the early to late 1970's, followed by a period of slower growth through 1982. In 1983 pesticide use declined sharply due to low crop prices, acreage diversion, and land retirement programs.<sup>18</sup> Since 1984 pesticide use has remained fairly stable. Table 3-5 presents annual agricultural pesticide use from 1986 to 1989.<sup>16</sup>

As can be seen in Tables 3-6 and 3-7, the overall increase in pesticide use can be attributed primarily to the increased use of herbicides. While insecticide use on the major crops decreased from 1964 to 1982, herbicide use increased by a factor of 6.5. The increase in total herbicide use is primarily due to a rise in the use of herbicides in corn, soybean, and cotton production. In the early 1950's, 10 percent of corn acreage was treated with herbicides. Today, herbicide treatment of corn has stabilized at 90 to 96 percent of the acres planted. Similar increases in the percentage of soybean and cotton areas receiving herbicide applications have occurred.<sup>19</sup>

Insecticide use has also grown since the 1950's, but not as dramatically as herbicide use. Because of the discovery of DDT

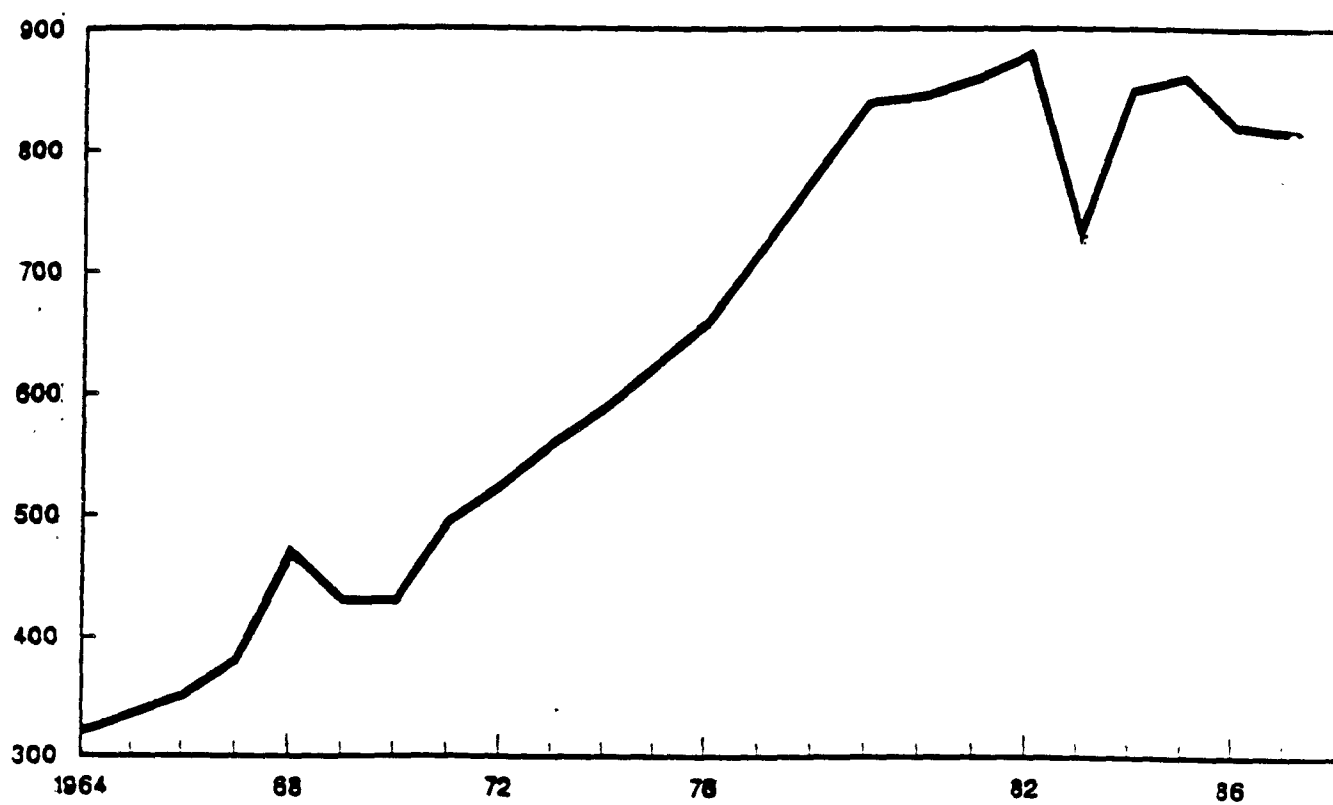


Figure 3-1. Total agricultural pesticide use in the United States in millions of pounds of active ingredients.

TABLE 3-5. ANNUAL U. S. AGRICULTURAL PESTICIDE USE<sup>16</sup>

Year	Million lb active ingredient <sup>a</sup>
1986	820
1987	815
1988	845
1989	806

<sup>a</sup>Includes herbicides, insecticides, and fungicides only.

TABLE 3-6. PESTICIDE USE ON MAJOR CROPS BY CLASS<sup>a-b,9,16</sup>  
(Million pounds active ingredients)

Year	Herbicides	Insecticides	Fungicides	Other <sup>c</sup>	Total
1964	70.5	116.7	5.8	31.7	224.7
1966	101.2	108.3	6.0	35.7	251.1
1971	213.1	127.9	6.4	29.8	377.2
1976	373.9	130.3	8.1	35.3	547.6
1982	455.6	71.2	6.6	24.3	557.7
1989	520	151	65	70	806

<sup>a</sup>Active ingredients, excluding sulfur and petroleum products.

<sup>b</sup>Major crops are cotton, corn, soybeans, sorghum, rice, tobacco, peanuts, wheat, other small grains, alfalfa, other hay, and pasture.

<sup>c</sup>Includes rodenticides, fumigants, and molluscicides; does not include wood preservatives, disinfectants, and sulfur.

TABLE 3-7. ANNUAL AGRICULTURAL USE OF HERBICIDES  
AND INSECTICIDES  
(Million pounds active ingredients)

Class of pesticide	1987 <sup>20</sup>	1988 <sup>9</sup>	1989 <sup>16</sup>
Herbicides	505 <sup>a</sup>	510	520 <sup>a</sup>
Insecticides	179 <sup>b</sup>	185	151 <sup>b</sup>
TOTAL	684	695	671

<sup>a</sup>Includes plant growth regulators.

<sup>b</sup>Includes miticides and contact nematicides.

in 1940 and the widespread use of it and other organochlorines, insecticide treatment was already well established in the 1950's on high-value crops (cotton, tobacco, potatoes, vegetables, fruits, and nuts). By the 1960's usage was fairly stable, and it has remained so through the 1970's and 1980's. As with herbicides, the greatest impact on insecticide usage has been the increase in insecticide applications to corn, from 10 percent of the planted corn acres in the 1950's to 35 to 40 percent in the mid-1970's. This increase has been offset somewhat, however, by the introduction of new compound classes of insecticides that have replaced the organochlorines. These classes of compounds, the organophosphates, carbamates, and pyrethroids, are effective at lower application rates than the organochlorines.

Table 3-8 shows total annual user expenditures on pesticides in the United States from 1979 to 1989. The agricultural sector represents approximately 75 percent of the conventional pesticide usage in the United States. The effects of a poor agricultural economy and an administrative freeze on farm programs are reflected in the total user expenditure figures for 1986. Both of these factors caused a decrease in pesticide demand, resulting in increased price competition between manufacturers. During this time pesticide manufacturers withdrew less profitable products from the market and cut prices on many name-brand products.<sup>21</sup> Since 1988, annual user expenditures have risen, primarily because of the rapidly increasing costs associated with developing new products today and increasing dealer costs, particularly the increasing cost of liability insurance.<sup>22</sup>

#### 3.4.2 Agricultural Pesticide Usage by Product and Crop

Table 3-9 lists the top 15 pesticides by volume used in the United States in 1989. As can be seen from the table, the top seven products are herbicides. The most popular herbicides in terms of volume used are the amides and triazines, while organophosphates dominate the insecticide market.

Table 3-10 lists the top 10 herbicides, insecticides, and other AI's (including fungicides) used on farms during 1991 for corn, cotton, peanuts, potatoes, rice, sorghum, soybeans, and

TABLE 3-8. U.S. ANNUAL USER EXPENDITURES  
ON PESTICIDES<sup>a</sup>

Year	Total expenditures, millions of dollars
1979	5,050
1980	5,800
1981	6,470
1982	6,470
1983	6,050
1984	6,783
1985	6,560
1986	6,490
1987	6,850
1988	7,380
1989	7,615

<sup>a</sup>Years 1979-1989 reference 16.

TABLE 3-9. ANNUAL USAGE ESTIMATES FOR THE LEADING AGRICULTURAL PESTICIDES BY VOLUME IN THE UNITED STATES (Approximate Values, 1989)<sup>a,16</sup>

Pesticide	Usage in million pounds active ingredient	Uses	Compound class
Atrazine	70-90	Herbicide	Triazine
Alachlor	60-75	Herbicide	Amide
2, 4-D	40-65	Herbicide	Phenoxy
Metolachlor	40-55	Herbicide	Amide
Trifluralin	30-40	Herbicide	Aniline
EPTC	20-30	Herbicide	Carbamate
Cyanazine	20-30	Herbicide	Triazine
Butylate	15-25	Herbicide	Carbamate
Carbaryl	10-15	Insecticide	Carbamate
Maneb/mancozeb	8-12	Fungicide	Dithiocarbamate
Glyphosate	8-13	Herbicide	Phosphono amino acid
Chlorpyrifos	8-16	Insecticide	Organophosphate
Methyl parathion <sup>b</sup>	8-12	Insecticide	Organophosphate

<sup>a</sup>The estimates represent all usage of the active ingredient including noncrop usage.

<sup>b</sup>The estimate does not include the pounds of ethyl parathion usage.

TABLE 3-10. APPLICATION OF PESTICIDES BY FIELD CROP

Field Crop (Quantities in 1,000 lb)											
Active ingredient	Corn	Upland cotton	Peanuts	Potatoes (fall)	Rice	Sorghum	Soybeans	Wheat			Total (x10 <sup>3</sup> lb)
								Winter	Durum	Spring	
Herbicides											
Atrazine	52,060					5,249					57,309
Alachlor	37,174					1,146	12,835				51,155
Metolachlor	38,792	380	1,045	243		2,195	7,625				50,280
Cyanazine	23,161	1,701				96					24,958
Trifluralin	111	5,589	71	29			16,324		348	281	22,753
EPTC	14,355			1,192							15,547
Pendimethalin	2,745	1,551	331	175	107		7,908				12,817
Butylate	8,478										8,478
2,4-D	2,800		152		130	269	133	1,540	533	2,361	7,918
Propanil					6,696						6,696
Insecticides											
Chlorpyrifos	6,716	718	460			130					8,024
Terbufos	5,986					144					6,130
Fonofos	2,890		79	42							3,011
Carbofuran	2,278			108	72	339					2,797
Phorate	1,306	193	117	1,119							2,735
Methyl parathion	812	1,528		7	91		205				2,643
Aldicarb		569	502								1,071
Acephate		583	26								609
Dicrotophos		440									440
Dicofol		423									423

TABLE 3-10. (continued)

Field Crop (Quantities in 1,000 lb)											
Active ingredient	Corn	Upland cotton	Peanuts	Potatoes (fall)	Rice	Sorghum	Soybeans	Wheat			Total (x10 <sup>3</sup> lb)
								Winter	Durum	Spring	
Other AI's											
Metam-sodium			1,917	12,351							14,268
Dichloropropene				8,431							8,431
Chlorothalonil			5,641	272							5,913
Tribufos		2,659									2,659
Ethephon		2,179									2,179
Mancozeb			31	1,415							1,446
Maneb				587							587
PCNB		479	67								546
Benomyl			7		196						203
Thidiazuron		143									143

Source: Agricultural Chemical Usage: 1991 Field Crop Summary. National Agricultural Statistics Service and Economic Research Service, U.S. Department of Agriculture, Washington, DC. March 1992.



wheat.<sup>23</sup> The crops shown in this table are among the major crops identified in Table 3-6, which reported total quantities of herbicides, insecticides, fungicides, and other pesticides. Comparison of the AI's and respective usage in Table 3-9 with those in Table 3-10 shows that the same high usage herbicides appear in both tables but for insecticides and lower volume usage herbicides, the two tables show significant differences. A contributing factor may be that the data in Table 3-9 represents all 1989 usage, including noncrop usage, whereas the data in Table 3-10 represent 1991 usage on specific crops.

#### 3.4.3 Trends in Agricultural Pesticide Use

It is difficult to predict the direction pesticide use will take in the near future because so many conflicting factors are involved. The increased use of conservation tillage practices mandated under the Food Security Act of 1985 and other Government farm policies are expected to produce an increase in pesticide use. The Integrated Pest Management Program, increased pressure from a more environmentally aware public, the Conservation Reserve Program, and the development of new pesticides that are effective at significantly lower application rates are expected to exert a negative influence on the volume of pesticides used. These positive and negative influences will probably offset each other, and pesticide use should remain fairly stable, as it did from 1987 to 1989 (Table 3-5).

There also are indications that pesticide manufacturers are changing formulations in response to safety and environmental concerns. Some emulsifiable concentrates are decreasing in availability as the manufacturer increases production of dry or water-based formulations. Emulsifiable concentrates currently on the market may be older products that are decreasing in market share for their designated uses due to the introduction of new products.<sup>24</sup>

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#### 4.0 EMISSION ESTIMATION METHODOLOGIES

Because various techniques may be used to reduce emissions from agricultural pesticide formulations, a way must be found to estimate the quantity of volatile organic compounds (VOC's) emitted under existing conditions. Emissions of VOC's from pesticide applications are the result of volatilization of the active ingredient (AI), organic solvents, emulsifiers, and other organic compounds that may be used in the formulation. For most States, data are not available for total emissions from pesticide application in ozone nonattainment areas and within the State in general. This section provides information on available sources of data for agricultural pesticide usage during the 1980's (1987-1989 for herbicides and 1982-1984 for insecticides), methods that can be used to estimate VOC emissions, and estimated nationwide total VOC emissions and VOC emissions in ozone nonattainment areas.

##### 4.1 BACKGROUND

Estimating VOC emissions from agricultural pesticide application requires data on total quantities applied by type of formulation. Information is available from the U. S. Environmental Protection Agency (EPA) Office of Pesticide Programs (OPP) for the total annual quantity of pesticide used in the United States, usage of selected pesticide classes on major crops, and annual estimates of use for the 15 leading AI's. However, very limited information is available for pesticide usage by major class by State, use of individual AI's (except for the top 15), use by type of formulation, or other detailed usage data. Only two sources of data were found that would provide sufficient detail to allow the estimation of VOC emissions.

These two sources were the Resources for the Future (RFF) data bases on herbicide usage (by county) and insecticide usage in each State and the Pesticide Use Report (PUR) compiled by county in California by the California Department of Pesticide Regulation (DPR).

#### 4.1.1 California Pesticide Usage

The DPR compiles data on an annual basis for the use of pesticides in each county of the State. This data compilation is the PUR. Until recently, the data were compiled only for a fixed list of restricted-use pesticide AI's composed of 38 insecticides, 18 herbicides, 6 nematocides, 2 adjuvants (substances added to aid the action of the AI), and 16 miscellaneous AI's and for pesticides applied by licensed commercial applicators. Data are currently collected for all pesticides used for agricultural purposes within the State; however, these data have recently been completed by DPR. In each county, farmers and commercial applicators provide selected information for each pesticide to the county, which in turn transmits the data to the DPR.

Currently, the California Department of Pesticide Regulation is developing a mapping system to track applications of pesticide products. Two data bases, the Product Label and Inert Ingredient data bases, will be able to retrieve the identities and weight percentages of active and inert ingredients in any California-registered pesticide product.

Appendix A provides a more detailed description of the PUR and selected tabular summaries of pesticide usage in California during 1987, the most recent year for which data was available. The PUR for 1990, which includes data for all pesticides and not just restricted-use AI's, became available in June 1992.

#### 4.1.2 Resources for the Future

The herbicide AI use information for nationwide emission estimates was obtained from the National Pesticide Use Inventory compiled by RFF. The insecticide information also came from RFF. There are no other data bases available to provide nationwide pesticide use information at a comparable level of

detail. Resources for the Future gathers information on pesticide use and compiles the information in a comprehensive data base format. Funding for the RFF studies comes from EPA, the U.S. Department of Agriculture (USDA), the National Oceanic and Atmospheric Administration (NOAA), and several pesticide manufacturers. Generally, the RFF data bases were created based on pesticide usage estimates calculated using two coefficients: the percent of acres that are treated and the average annual application rate per treated acre.<sup>1</sup> These coefficients are typically provided in terms of Statewide average use for a particular AI and crop combination. The only data available from RFF are 1987-1989 for herbicides and 1982-1984 for insecticides. The number of treated acres is estimated by multiplying the percent of acres treated by estimates of the number of planted crop acres reported in the 1982 Census of Agriculture for insecticides or in the 1987 Census of Agriculture for herbicides. The number of treated acres is multiplied by the application rate per acre to estimate the total poundage of AI that is used on the crop in a county.

Information on herbicides is available on the county level, allowing analysis of herbicide use in ozone nonattainment areas. Insecticide and fungicide data is currently available only on the State level. No information on other types of pesticides has been collected for the data base. However, herbicides, insecticides, and fungicides account for 93 percent of the U.S. pesticide market, and herbicides represent the largest volume of pesticide used annually.<sup>2</sup> Therefore, the data base contains the majority of agricultural pesticide use information.

#### 4.1.3 RFF Data Base Summary

According to the data base, 511 million pounds (255,600 tons) of AI's were applied nationwide to cropland. Because of the time period for which data are available, several of the AI's included in these data bases are no longer registered and in use. Herbicides accounted for over 84 percent of pesticide use (424 million pounds [211,800 tons] of AI's). Insecticide use amounted to 87.5 million pounds (43,800 tons) of

AI's. The States with the largest contributions overall to total pesticide use were Iowa, Illinois, Minnesota, Texas, and California. For these States the majority of pesticide use (85 percent or greater) is due to use of herbicides. Data base information on the top four States indicates that the largest volume of herbicide AI used in each of the States is those AI's including atrazine, metolachlor, and alachlor used primarily to control weeds in corn. The top three States contributed one percent or less to the nationwide insecticide use. California insecticide use (15 million pounds [7,500 tons] of AI's), however, accounted for greater than half of the State's pesticide use. In the 1982-1984 RFF data base for insecticides, this was largely a result of the use of dibromochloropropane (DBCP), which accounted for 65 percent of California's insecticide use. According to California DPR, the use of DBCP in California was suspended in 1977. Dibromochloropropane was a soil fumigant used to treat a variety of crops including citrus, berries, grapes, cotton, vegetables, and ornamentals. The registrations for all DBCP products were cancelled in 1985 as a result of an Office of Pesticide Programs (OPP) special review. The special review determined that the benefits of DBCP did not outweigh its risks which were identified as oncogenicity, mutagenicity, reproductive effects and impacts on ground water. Telone®, dazomet and metam are fumigants that may have been used as substitutes for DBCP. The next-highest insecticide-using State is Georgia, with a total of 11.9 million pounds for the 14 AI's reported in the data base. In this case, DBCP and ethylene dibromide (EDB), a fumigant that had all agricultural uses cancelled in 1990, accounted for 17.9 percent and 27.1 percent of the total insecticide use, respectively. Fumigant substitutes for EDB include Telone®, methyl bromide, chloropicrin, and metam. Thus, approximately 45 percent of the insecticide use in Georgia has been eliminated or likely replaced with other insecticides.

The highest herbicide use in ozone nonattainment areas was found in California (12.2 million pounds [6,100 tons] of AI's), which has 35 counties with whole or partial nonattainment status.

The AI's with the highest use in California were dimethyl tetrachloroterephthalate (DCPA) (1.1 million pounds [550 tons]), molinate (0.97 million pounds 485 tons]), and glyphosate (0.96 million pounds [480 tons]). The State with the next-highest herbicide use in ozone nonattainment areas is Michigan (11.2 million pounds [5,600 tons] of AI's,) which has 37 counties with whole or partial ozone nonattainment status. The AI's with the highest use in Michigan were atrazine (2.4 million pounds [1,200 tons]), metolachlor (1.9 million pounds [950 tons]), alachlor (1.4 million pounds [700 tons]), and S-ethyl dipropylthiocarbamate (EPTC) (1.1 million pounds [550 tons]). Together California and Michigan account for 41 percent of the herbicide use in ozone nonattainment areas nationwide. It should be noted that Pennsylvania has the highest number of counties with ozone nonattainment status (41) and accounted for approximately 8 percent of the herbicide use in ozone nonattainment areas nationwide. Connecticut, Rhode Island, Massachusetts, and New Jersey were listed entirely as ozone nonattainment areas such that 100 percent of these States' pesticide use was in ozone nonattainment areas.

#### 4.1.4 U.S. Department of Agriculture Data

The U. S. Department of Agriculture (USDA) publishes an annual summary of the usage of agricultural chemicals in ten selected field crops in the United States. Usage data for 1991 were presented in Section 3, Table 3-10 for the top 10 herbicides, insecticides, and other active ingredients for each of the field crops. The 1991 Field Crops Summary reported a total of 308 million pounds of herbicides, 33 million pounds of insecticides, and 37 million pounds of other active ingredients, including soil fumigants, fungicides, and others. These data present a more accurate summary of the current AI usage on specific crops than the RFF data base. However, these data cannot be used to estimate nationwide usage or emissions because they represent usage only on selected crops and are not representative of total agricultural usage. In addition, no data are available for usage in ozone nonattainment areas; this



information is available in the RFF data. Therefore, the RFF data will be used throughout this document to estimate total AI usage and VOC emissions due to solvent loss.

#### 4.2 VOC EMISSION CALCULATION METHODS

In general, the information necessary to calculate VOC emissions from pesticide application includes an estimate of pesticide use (pounds or tons of organic AI's); the formulations of the AI's used, including the percent content of AI, organic solvents, and other VOC inert constituents; and the percent of the AI used in each type of formulation, i.e., liquid, granular, etc. Additional required information includes the application transfer efficiency, sorption and degradation losses, and other fate estimates that are appropriate. Possible methods that can be used to measure the organic solvent content of formulations or to estimate VOC emissions are discussed in the following subsections.

##### 4.2.1 Laboratory Test Method

A test method development program was funded by the EPA Office of Air Quality Planning and Standards (OAQPS) to develop two test procedures for pesticide formulations. These test procedures were developed to determine the organic solvent content of emulsifiable concentrates (EC's) and liquid, non-EC formulations of pesticides. The two test procedures are based on thermal methods so the "organic solvent" content measured will contain the actual solvent plus other formulation components that will volatilize at 54°C. The two methods selected were the Volatile Organic Pesticide (VOP) Method, which is a purge and trap procedure, and ASTM E1131-86, thermal gravimetric analysis (TGA). Each of the test methods is briefly described in this section; additional information and the test procedures are presented in Appendix C.

4.2.1.1 VOP Method Summary. The VOP Method is a test method that allows direct measurement of the volatile organics in a pesticide formulation. The procedure involves the dry nitrogen purge of volatile organics in the pesticide formulation from a weighed sample at a preselected temperature (54°C) and adsorption

of these organics onto activated charcoal in preweighed tubes. Any water, methanol, or other weakly adsorbed compound (e.g., ethanol, acetone, acrolein) will pass through the charcoal and be adsorbed in preweighed tubes filled with adsorber material (e.g., Drierite). The sample is heated for a selected period of time and, at the conclusion of the heating period, the final adsorption weights for the sample residue, the charcoal tubes, and the water tubes are determined. The weight percent organic solvent and water in the pesticide formulation is determined from the weight differential. The organic solvent content calculated will contain solvent plus other constituents of the formulation that volatilize at less than or equal to 54°C.

Use of this method has the advantage of requiring a relatively inexpensive apparatus to perform the test. Because the organic solvent can be desorbed from the activated charcoal, analyses can be performed to determine if any active ingredient is being evolved or identify the compounds evolved as organic solvent.

The VOP Method requires a relatively large (1 gram) sample compared to the TGA method and, although it is probably not a major concern, the sample size presents more of a potential safety and waste disposal concern than the smaller TGA samples. Another disadvantage would be the potential diminished accuracy of the method for low organic solvent content pesticide formulations and for organic compounds with poor adsorption properties on carbon.

**4.2.1.2 TGA Summary.** Thermal gravimetric analysis (TGA) is a technique in which the mass of the pesticide formulation is continuously measured as a function of time or temperature. During this measurement, the formulation is subjected to a controlled temperature program and a constant flow of dry nitrogen gas. Mass loss over specified temperature ranges can provide a compositional analysis of the pesticide formulation (e.g., organic solvent content, other VOC's). In this method, a small quantity of the formulation (10 to 30 milligrams [mg]) is placed in a sample holder in the apparatus and the heating

program initiated. The change in mass is continuously recorded over the selected temperature range. Mass loss can be recorded as a function of increasing temperature or as a function of time at a preselected temperature. Establishment of a mass loss plateau can indicate the completed evolution of organic solvents in the formulation at the selected temperature.

There are several advantages to the use of TGA, including:

1. The method can be a highly accurate procedure;
2. Instrumentation can be readily purchased or commercial laboratories are available to perform TGA analyses;
3. The method is relatively simple to perform; and
4. This procedure uses small quantities of sample, thus minimizing safety and waste disposal concerns.

There are two major disadvantages to this method. If equipment purchase is considered, the TGA apparatus is relatively expensive (e.g., \$40,000 to \$50,000) so use of commercial laboratories may be necessary. The second major disadvantage is the inability to determine if an active ingredient is being evolved. Because the evolved compounds are not collected, no analysis can be performed to determine if the active ingredient is being volatilized. The water content of the formulation is usually determined by using Karl Fischer reagent or gas chromatography.

#### 4.2.2 The CARB Method for VOC Emission Estimate Calculations

The DPR's PUR contains use and formulation data for nonrestricted-use and restricted-use pesticides (those pesticides that must be applied by a certified applicator) in California (see Appendix A). Results from a California Air Resources Board (CARB) survey on statewide use of pesticide oils (e.g., carrot oil, weed oil) were used to determine the usage of nonsynthetic pesticides, which are not reported in the PUR. Mr. Bill Lovelace of CARB provided the 1987 statewide pesticide VOC emission estimate at a meeting of the CAPCOA Pesticide Solvent Task Force in Sacramento in March 1990. The estimated emissions for synthetic pesticides were about 32,100 tons/yr (88 tons/d) and nonsynthetic pesticides were about 18,600 tons/yr (51 tons/d).

Estimation methods for emissions due to pesticide application have been published by CARB.<sup>3</sup>

4.2.2.1 Emissions Due to Active Ingredients. In calculating emissions, CARB assumed that there were no VOC emissions from inorganic pesticides or from organic pesticides with low vapor pressures ( $<10^{-7}$  millimeters of mercury [mm Hg]). Additional factors related to the type of application were also considered in calculating emissions, including:

1. Nonacreage application;
2. Applications to vegetated surfaces; and
3. Incorporation of a pesticide after application.

Prior to 1990, the CARB usage data did not necessarily include nonrestricted-use pesticides. Only commercial applicators were required to report nonrestricted-use pesticide applications. A grower may or may not have reported use of a nonrestricted-use pesticides. A correction factor was developed from information obtained from county agricultural staff to correct for under reporting. Based on pesticide use permit information supplied by DPR, it was determined that a correction factor should be applied to all reported restricted-use pesticide applications to compensate for underreporting. Subsequent to 1990, the California Pesticide Use Report will include data for all types of pesticides, restricted and nonrestricted.

The VOC emissions were estimated beginning with emissions during application due to immediate evaporation. Losses to the remaining applied pesticide were estimated including loss due to adsorption and absorption, and due to degradation. For most pesticides, only a small percentage is irreversibly adsorbed and unavailable for evaporation. Most pesticides are susceptible to one or more degradation mechanisms, however, the quantity of hydrocarbons available for vaporization is not necessarily reduced. A pesticide may be degraded into two smaller compounds, but this does not change the total mass available for evaporation. Each of these losses were assumed to be small but were considered in estimating VOC emissions.

An evaporation rate is needed to calculate the VOC emissions per month from the amount of pesticide applied. The method used by CARB to estimate the evaporation rate was based on a model developed by Hartley and modified by Spencer.<sup>4,5</sup> The method is based on the principle that the rate of loss of a pure substance into the atmosphere from an inert surface is governed by two of the substance's properties: the saturation vapor concentration and the rate of diffusion through the still air layers bounding the treated surface. Emission rates of pesticides applied to soil surfaces, incorporated into the soil, and applied to vegetation differ and VOC emissions were calculated separately for each type of application (see Appendix A for details).

4.2.2.2 Emissions Due to Inert Ingredients. Many pesticide formulations, particularly emulsifiable concentrates, contain volatile organic solvents classified as inert ingredients. Emissions of these compounds have not been estimated because of the difficulties imposed by claims of confidentiality of the pesticide formulations. Emissions calculated have traditionally been based on the amount of AI applied. Because the pesticide usage in California is reported as the total amount of formulation applied, the amount of AI applied was derived for this document from the percent content of AI reported by the registrant of a formulation. Midwest Research Institute (MRI) reviewed formulation data at the OPP in Washington, D.C., and developed the inert content information. The amount of inert applied was estimated by taking the appropriate percentage of the total formulation applied. Using the 1987 PUR in California, the estimated emission of inert (solvent) ingredients was approximately 3,100 tons/yr (see Appendix A, Tables A-4 and A-5).

Unfortunately, calculating emissions from the inert portion of the formulation is not as simple as taking the remaining percentage of the total applied and using the same method as that used for the AI because many different compounds and materials are used as inerts in a formulation. Many of these compounds are inorganic and are not a source of emissions. In order to determine emissions from the inert portion of a pesticide, the

identity and percentage of the VOC's in the formulation must be known. If the identities of inerts are known, then their vapor pressures can be used to calculate the maximum evaporation rate as described in Appendix A. If the percentage of the inert is known, then the total amount applied can be calculated from the total usage reported in the PUR. This is the approach used in the CARB emission inventory.

States may find data developed by the CARB VOC emissions estimates useful in their estimates of VOC emissions. Average data, such as percent of AI in each formulation, from the California PUR may be used as estimates in calculations to approximate another State's VOC emissions.

4.2.2.3 Nonsynthetic Data. The CARB also estimated VOC emissions for nonsynthetic pesticides or pesticide oils (i.e., weed oils, carrol oil). Insecticidal oils are important because one treatment with an oil can often replace more than one spray application of a pesticide. The usage estimate, 18,600 tons of pesticide oils, was obtained from a statewide inventory conducted by CARB in 1980 of oils used as pesticides in 1979. Emissions from nonsynthetic pesticides were calculated by the CARB method described in Section 4.2.2.

#### 4.2.3 Use of Formulation Data

The method used in this document (Section 4.3) to calculate nationwide total VOC emissions and emissions from ozone nonattainment areas using the RFF data bases makes several assumptions not made in the CARB method. No correction factors were applied to account for underreporting of pesticide use. The VOC emissions are presented for total pesticides: AI's and inerts.

4.2.3.1 Active Ingredients. The estimation of VOC emissions from a pesticide formulation ready for field application is very difficult because of the lack of experimental data on losses resulting from field application. As an example, volatilization losses of pesticide formulation components during the actual application process represents an area where few experimental data exist and studies in this area are only in the

formative stages for cooperative studies between the U. S. Department of Agriculture (USDA) and industry.<sup>6</sup> Studies have been conducted on the losses due to drift during aerial application. The determination of actual losses due to volatilization during application is complicated by the fact that the evaporation is continuous from the time the formulation leaves the spray boom and the overall process is best regarded as a continuous, rapid, and dynamic system.<sup>7-9</sup>

In an attempt to obtain some insight into the magnitude of pesticide losses during and subsequent to field application, the available literature was reviewed. A summary of these pesticide volatilization studies is presented in Table 4-1. This summary includes data for 16 different AI's applied primarily by some type of vehicle drawn sprayer (surface sprayer), although some data are included for aerial application. Because this summary focussed on volatilization, numerous studies on drift resulting from aerial application have not been included. Soil types ranged from sandy loam to clay with moisture levels ranging from dry to wet. Because of the number of AI's and formulations, the results showed the expected very wide range of volatilization. The data shown in Table 4-1 were divided into three time groups: (1) losses upon application and for up to 24 hours after application; (2) losses during application and subsequent cumulative time intervals between 1 day and 7 days; and (3) losses during application and for subsequent cumulative times of 21 days to 30 days. For surface sprayers, the results show that the simple arithmetic average volatilization losses during application and for periods up to 24 hours after application were 41 percent. The average losses during application and for times greater than 1 day but not over 7 days after application were 55 percent. Losses during application and for times greater than 21 days but not over 30 days after application averaged 65 percent. There is a very large variance in the percent losses within each of these three groupings. The vapor pressures of the AI's ranged from approximately  $10^{-2}$  to  $10^{-7}$  but the majority were in the range of  $10^{-4}$  to  $10^{-6}$ . However, the results indicate that

TABLE 4-1. SUMMARY OF PESTICIDE VOLATILIZATION STUDIES

Active ingredient	Vapor pressure (mm Hg) <sup>a</sup>	Formulation type	Application method	Soil type	Volatilization	Reference
Dieldrin	$9.9 \times 10^{-6}$	Aq. emul.	Surface Spray	Silt loam	43%; Application	1
Heptachlor	$3 \times 10^{-4}$	Aq. emul.	Surface Spray	Silt loam	43%; Application	1
2,4-D	$8 \times 10^{-6}$	Aq. soln.	Surface Spray	Not stated	1-8%; Application	2
Toxaphene	$4 \times 10^{-6}$	Aq. emul.	Surface Spray	Not stated	17%; Application	3
Toxaphene	$4 \times 10^{-6}$	Aq. emul.	Surface Spray	Not stated	54%; Application	3
DDT	$1.5 \times 10^{-7}$	Aq. emul.	Surface Spray	Not stated	72%; Application	3
Zinophos	$3 \times 10^{-3}$	Aq. emul.	Surface Spray	Silt loam	46%; Application	4
Dyfonate	$2.1 \times 10^{-4}$	Aq. emul.	Surface Spray	Silt loam	13%; Application	4
Dimethoate	$2.5 \times 10^{-5}$	Aq. emul.	Surface Spray	Sandy loam	16%; Application	5
Dieldrin	$9.9 \times 10^{-6}$	Aq. emul.	Surface Spray	Sandy loam	72%; 12 hr <sup>b</sup>	6
Heptachlor	$3 \times 10^{-4}$	Aq. emul.	Surface Spray	Sandy loam	87%; 12 hr <sup>b</sup>	6
Trifluralin	$1.1 \times 10^{-4}$	Aq. emul.	Surface Spray	Moist silt loam	50%; 5 hr	7
Heptachlor	$3 \times 10^{-4}$	Aq. emul.	Surface Spray	Moist silt loam	50%; 6 hr	7
Lindane	$3.3 \times 10^{-5}$	Aq. emul.	Surface Spray	Moist silt loam	50%; 6 hr	7
EPTC	$3.4 \times 10^{-2}$	Aq. soln.	Surface Irrig.	Clay loam	55%; 24 hr	8
EPTC	$3.4 \times 10^{-2}$	Aq. soln.	Surface Spray	Dry sandy loam	20%; 15 min	9
EPTC	$3.4 \times 10^{-2}$	Aq. soln.	Surface Spray	Dry sandy loam	23%; 24 hr	9
EPTC	$3.4 \times 10^{-2}$	Aq. soln.	Surface Spray	Moist sandy loam	27%; 15 min	9
EPTC	$3.4 \times 10^{-2}$	Aq. soln.	Surface Spray	Moist sandy loam	49%; 24 hr	9



TABLE 4-1. (continued)

Active ingredient	Vapor pressure (mm Hg) <sup>a</sup>	Formulation type	Application method	Soil type	Volatilization	Reference
EPTC	$3.4 \times 10^{-2}$	Aq. soln.	Surface Spray	Wet sandy loam	44%; 15 min	9
EPTC	$3.4 \times 10^{-2}$	Aq. soln.	Surface Spray	Wet sandy loam	69%; 24 hr	9
2,4-D	$8 \times 10^{-6}$	Aq. soln.	Surface Spray	Not stated	25-30%; 30 min	10
2,4-D (butyl ester)	---	Aq. soln.	Surface Spray	Not stated	30-40%; 2 hr	2
2,4-D (octyl ester)	---	Aq. soln.	Surface Spray	Not stated	10-15%; 2 hr	2
Toxaphene	$4 \times 10^{-6}$	dust	Aerial	Not stated	86%; Application <sup>c</sup>	11
Toxaphene	$4 \times 10^{-6}$	Aq. emul.	Aerial	Not stated	52%; Application <sup>c</sup>	11
Methoxychlor	---	Aq. emul.	Aerial	Not stated	47%; Application <sup>c,d</sup>	11
Dieldrin	$9.9 \times 10^{-6}$	Aq. emul.	Surface Spray	Sandy loam	89%; 30d	6
Heptachlor	$3 \times 10^{-4}$	Aq. emul.	Surface Spray	Sandy loam	96%; 30d	6
2,4-D	$8 \times 10^{-6}$	Aq. soln.	Surface Spray	Clay/silt	21%; 5d	12
Trifluralin	$1.1 \times 10^{-4}$	Aq. emul.	Surface Spray	Moist silt loam	90%; 7d	7
Heptachlor	$3 \times 10^{-4}$	Aq. emul.	Surface Spray	Moist silt loam	90%; 6d	7
Chlordane	$1 \times 10^{-5}$	Aq. emul.	Surface Spray	Moist silt loam	50%; 2.5d	7
Dacthal	$2.5 \times 10^{-6}$	wet powder	Surface Spray	Moist silt loam	2%; 1.5d	7
Trifluralin	$1.1 \times 10^{-4}$	Aq. emul.	Surface Spray	Moist silt loam	90%; 7d	7
Lindane	$3.3 \times 10^{-5}$	Aq. emul.	Surface Spray	Moist silt loam	90%; 6d	7
Trifluralin	$1.1 \times 10^{-4}$	Aq. emul.	Surface Spray	Dry sandy loam	2-25%; 2d	7
Heptachlor	$3 \times 10^{-4}$	Aq. emul.	Surface Spray	Dry sandy loam	14-40% 2d	7
Chlordane	$1 \times 10^{-5}$	Aq. emul.	Surface Spray	Dry sandy loam	2%; 2d	7

TABLE 4-1. (continued)

Active ingredient	Vapor pressure (mm Hg) <sup>a</sup>	Formulation type	Application method	Soil type	Volatilization	Reference
Lindane	$3.3 \times 10^{-5}$	Aq. emul.	Surface Spray	Dry sandy loam	12%; 2d	7
EPTC	$3.4 \times 10^{-2}$	Aq. soln.	Surface Irrig.	Clay loam	74%; 2.25d	8
Toxaphene	$4 \times 10^{-6}$	Aq. emul.	Aerial	Not stated	25%; 5d	13
Triallate	$1.1 \times 10^{-4}$	Aq. emul.	Surface Spray	Clay	70-100%; 5d	14
Trifluralin	$1.1 \times 10^{-4}$	Aq. emul.	Surface Spray	Clay	61-79%; 5d	14
EPTC	$3.4 \times 10^{-2}$	Aq. soln.	Surface Spray	Dry loam/sand	44%; 6d	9
EPTC	$3.4 \times 10^{-2}$	Aq. soln.	Surface Spray	Moist loam/sand	68%; 6d	9
EPTC	$3.4 \times 10^{-2}$	Aq. soln.	Surface Spray	Wet loam/sand	90%; 6d	9
DCPA	$2.5 \times 10^{-6}$	Wet powder	Surface Spray	Yolo	10%; 21d	15
Trifluralin	$1.1 \times 10^{-4}$	Aq. emul.	2.5cm Soil Inc.	Cecil soil	3.5%; Application	16

<sup>a</sup>Wauchope, R.D., T.M. Butler, A.G. Hornsby, P.W.M. Augustijn - Beckers, and J.P. Burt. The SCS/ARS/CES Pesticide Properties Database for Environmental Decision-Making. In: Reviews of Environmental Contamination and Toxicology; G.W. Ware, Editor. Volume 123. Springer-Verlag, New York. 1992. (Primary source).

<sup>b</sup>Includes losses upon application.

<sup>c</sup>Includes losses due to drift during application.

<sup>d</sup>Average of 15 separate studies over a 5 year period using methoxychlor applied at temperatures ranging from 2°C to 41°C.

TABLE 4-1. (continued)

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the highest percentage loss occurs during application and within the first 24 hours after application. After this initial period, the loss due to volatilization appears to slow markedly with time. After a 30 day period, the losses resulting from application and the subsequent 30 days showed an average of 65 percent compared to a 41 percent loss during application and the next 24 hours. For time periods in excess of 30 days, many other factors, including sorption, microbial degradation, hydrolysis, photolysis, and others, can lead to the loss of pesticide formulations which do not necessarily result in VOC emissions. Although the data show a wide variation, no other results are readily available to estimate VOC emissions from pesticide formulations. The remaining portion of the pesticide formulation will undergo sorption, surface water runoff, and natural degradative processes.

4.2.3.2 Solvents. Information was collected through an informal survey of manufacturers of the major types of formulations for the most used AI's by pounds used reported in the data bases. Formulations with organic solvents were assumed to consist of only AI and solvent and no other inert ingredients such that 100 percent of the formulation by weight is accounted for by AI and solvent. The percent of AI in organic solvent-containing formulations and the percent organic solvent content of those formulations were used to calculate VOC emissions due to organic solvents in pesticides.

The factors used to calculate VOC emissions from the pesticide use data obtained from RFF and from an informal survey of pesticide manufacturers are nationwide pounds of AI used, the fraction of AI production in a nonaqueous solvent-based formulation, and the fraction of the formulation that is nonaqueous solvent.<sup>1,10-25</sup> Calculations are discussed in more detail in Section 4.3. Results are discussed in Section 4.4.

Formulation information obtained from manufacturers describes current pesticide formulations and, therefore, is not necessarily representative of formulations used in the mid-1980's that are reported in the data bases. The registrations of

several AI's, (i.e., EDB, DBCP, etc.), have been cancelled since the data base was compiled, and no formulation information was obtained for these pesticides. However, since fumigants are highly volatile, 100 percent of the pounds used was added to the VOC emissions estimate. Cancelled nonfumigant pesticides were not considered in the emissions calculations because no information on their formulations was readily available from manufacturers and no assumptions were made concerning their volatilities. No formulation data was obtained for 51 percent of the insecticide usage data. Ninety three percent of the herbicide usage data was used in the emissions calculations and formulation data were available on 87 percent of that herbicide usage.

States that currently have no pesticide use data may obtain pesticide use data for that State from RFF. This information may be used to calculate VOC emissions estimates from data presented in Section 4.4 on percent of AI in organic solvent-based formulations and the percent of organic solvent content of the formulation.

States that have compiled pesticide use information by AI may estimate VOC emissions by using data presented in Section 4.4. However, information presented here may not cover all pesticides used by States and all use patterns. The selection and use of formulation types is specific to certain crops and geographic regions. Therefore, more specific information than that presented in Section 4.4 may be necessary to provide a more accurate estimate of VOC emissions.

Users of this method and data should be aware of the assumptions made as discussed above. The assumptions were made to simplify calculations due to the wide range of chemical and physical properties of the organic solvents and AI's, the lack of available data to characterize these properties, and the complete AI formulations. More specific information such as meteorological conditions and precise formulation information will allow more representative VOC emissions estimates to be calculated (e.g., by the CARB method). State or local agencies

should conduct a survey of pesticide use in their area to estimate their VOC emissions from pesticide application. An area survey would focus on only those pesticides and formulations used locally and would provide more accurate emissions estimates than using the data presented in this document.

With the availability of pesticide use inventory information, a more accurate VOC estimation can be made. Formulator data or pesticide analysis can be applied to the use data to more accurately represent VOC emissions due to pesticide application within the State.

#### 4.3 ESTIMATION EQUATION

The calculation of VOC emissions is based on the percentages of AI and organic solvent content of the pesticide formulations. The fraction of the AI formulated in an organic solvent-based formulation was applied to the nationwide total pounds of AI used to calculate the pounds of AI formulated in the organic solvent-based formulation. Using this figure and the percent of organic solvent in the formulation, the number of pounds of organic solvent associated with each AI was calculated using the following equation:

$$Z = \frac{X * Y}{1 - Y} \quad (\text{Eq. 1})$$

where:

X = AI pounds in organic solvent formulation;

Y = weight fraction of organic solvent in the formulation of the specific AI; and

Z = pounds of volatile organics formulated with the AI, volatile emissions per AI.

The maximum VOC emissions were estimated by adding the total pounds of an AI to Z

$$\text{Maximum VOC emissions} = Z + S, \quad (\text{Eq. 2})$$

where:

S = specific AI pounds used nationwide.

Total herbicide and insecticide solvent or maximum VOC emissions were estimated by totalling each for AI's used either nationwide or in ozone nonattainment areas. The combined total solvent and maximum VOC emissions are the sums of herbicide and insecticide totals.

#### 4.4 ESTIMATED VOC EMISSIONS

The VOC emissions estimates due to solvent usage were calculated by pesticide type--herbicide and insecticide-- nationwide and for ozone nonattainment areas in the United States using data from the RFF data bases (see Section 4.1.2). Nationwide the combined (herbicide plus insecticide) estimated maximum AI usage and solvent VOC emissions from agricultural use are 511 million pounds (255,600 tons) and 93 million pounds (46,400 tons), respectively. Solvent VOC emissions are defined as those emissions due only to the nonaqueous (organic) solvent in the formulation. Aqueous-based formulations may also contain organic constituents that could result in VOC emissions; however, for these calculations only nonaqueous-based formulations were considered. In ozone nonattainment areas, the approximated combined maximum AI usage is 72 million pounds (36,000 tons). The approximated combined solvent VOC emissions are 9.6 million pounds (4,800 tons).

Insecticide-related VOC emissions for the period 1982-1984 were calculated on a nationwide basis (Table 4-2) and approximated for ozone nonattainment areas (Table 4-3) from the ratio of herbicide use in state ozone nonattainment areas to herbicide use statewide. This approximation was necessary because insecticide use data was not available at the county level from RFF. The use patterns of herbicides and insecticides may be quite different within States so the results obtained by this method should be considered only rough approximations. The estimated VOC emissions in Tables 4-2 and 4-3 are only for the years 1982-1984 because this represents the time period of the RFF data base (see Section 4.1.2). Because of this, some of the AI's shown in these tables are no longer registered or in use. Table 3-10 presents a summary of the top ten herbicides,

TABLE 4 - 2. NATIONWIDE SOLVENT VOC EMISSION ESTIMATES FOR INSECTICIDE FORMULATIONS

Active ingredient	Pounds AI used <sup>a</sup>	Notes and formulation designation (EC and L)	Fraction AI in nonaqueous solvent formulation <sup>b</sup>	Pounds AI in nonaqueous solvent formulation <sup>c</sup>	Formulation nonaqueous solvent fraction <sup>b</sup>	Solvent VOC emissions estimates, pounds <sup>d</sup>
DBCP	29,072,029 <sup>e</sup>	f	0.00	0	0.00	
EDB	12,409,524 <sup>e</sup>	f	0.00	0	0.00	
Carbaryl	8,620,584		0.00	0	0.00	
Methyl parathion	7,650,238	EC <sup>g</sup>	1.00	7,650,238	0.40	5,100,159
Carbofuran	7,154,396	h		0		
Dinoseb	6,846,644 <sup>e</sup>		0.00	0	0.00	
Aldicarb	5,317,156		0.00	0	0.00	
Ethoprop	2,486,933	L	0.30	746,080	0.50	746,080
Methomyl	2,345,308	L <sup>g</sup> i	0.75	1,758,981	0.00	
Disulfoton	2,021,997	h		0		
Diazinon	1,842,044	L <sup>g</sup> i	0.75	1,381,533	0.30	592,086
Lindane	561,045 <sup>e</sup>		0.00	0	0.00	
Oxamyl	410,083	L <sup>g</sup> i	0.75	307,562	0.30	131,812
Fenamiphos	406,622	h		0		
2,3,5-T	386,698 <sup>e</sup>	h		0	0	0
Totals:						
Pounds	87,531,301			11,844,394		6,570,137
tons	43,766			5,922		3,285
Percent of total	49					
Percent of total cancelled	51					

<sup>a</sup>RFF data base (1982-1984).<sup>b</sup>Estimate from manufacturers.<sup>c</sup>Total use multiplied by percent use of nonaqueous solvent formulation.<sup>d</sup>Estimated emissions due to nonaqueous solvent.<sup>e</sup>Registration for agricultural uses have been cancelled.<sup>f</sup>Fumigant.<sup>g</sup>Percent solvent and/or percent formulation used is the average of a range.<sup>h</sup>No data were obtained from manufacturers.<sup>i</sup>Fraction of AI in nonaqueous solvent formulation is unknown, estimated to be 0.75.



TABLE 4-3. OZONE NONATTAINMENT AREA SOLVENT VOC EMISSION ESTIMATES  
FOR INSECTICIDE FORMULATIONS

Active ingredient	Pounds AI used <sup>a</sup>	Notes and formulation designation (EC and L)	Fraction AI in nonaqueous solvent formulation <sup>b</sup>	Pounds AI in nonaqueous solvent formulation <sup>c</sup>	Formulation nonaqueous solvent fraction <sup>b</sup>	Solvent VOC emissions estimates, pounds <sup>d</sup>
DBCP	6,640,051 <sup>e</sup>	f	0.00	0	0.00	
EDB	2,834,355 <sup>e</sup>	f	0.00	0	0.00	
Carbaryl	1,968,941		0.00	0	0.00	
Methyl parathion	1,747,314	EC <sup>g</sup>	1.00	1,747,314	0.40	1,164,876
Carbofuran	1,634,064	h		0		
Dinoseb	1,563,773 <sup>e</sup>		0.00	0	0.00	
Aldicarb	1,214,438		0.00	0	0.00	
Ethoprop	568,015	L	0.30	170,405	0.50	170,405
Methomyl	535,668	L <sup>g</sup> i	0.75	401,751	0.00	
Disulfoton	461,824	h		0		
Diazinon	420,723	L <sup>g</sup> i	0.75	315,542	0.30	135,232
Lindane	128,143 <sup>e</sup>		0.00	0	0.00	
Oxamyl	93,663	L <sup>g</sup> i	0.75	70,247	0.30	30,106
Fenamiphos	92,872	h		0		
2,3,5-T	88,322 <sup>e</sup>	h		0		
Totals:						
Pounds	19,992,149			2,705,260		1,500,619
tons	9,996			1,353		750
Percent of total	49					
Percent of total cancelled	51					

<sup>a</sup>Estimated from ratio of herbicide use in nonattainment and to nationwide herbicide use from RFF data base.

<sup>b</sup>Estimate from manufacturers.

<sup>c</sup>Total use multiplied by percent use of nonaqueous solvent formulation.

<sup>d</sup>Estimated emissions due to nonaqueous solvent.

<sup>e</sup>Registration for agricultural uses have been cancelled.

<sup>f</sup>Fumigant.

<sup>g</sup>Percent solvent and/or percent formulation used is the average of a range.

<sup>h</sup>No data were obtained from manufacturers.

<sup>i</sup>Fraction of AI in nonaqueous solvent formulation is unknown, estimated to be 0.75.

insecticides, and other AI's used for selected field crops in 1991.

The estimated maximum insecticide use (AI only) nationwide are 87.5 million pounds (43,800 tons), or 17 percent of the nationwide combined (herbicide plus insecticide) estimated AI usage. Insecticide-related solvent VOC emissions nationwide are estimated to be 6.6 million pounds (3,300 tons), or 7 percent of the nationwide combined VOC solvent emissions. As noted above, an approximation of individual insecticide AI use was made for ozone nonattainment areas. Table B-1 in Appendix B presents the statewide and State ozone nonattainment area data for insecticide use calculated from the corresponding ratios of herbicide use. The individual insecticide AI usages in Table 4-3 were calculated from the overall ratio (0.2284) of insecticide use nationwide and in ozone nonattainment areas that results from Table B-1. Approximate ozone nonattainment maximum AI usage was 20 million pounds (10,000 tons), or 4 percent of the nationwide combined maximum AI usage. Solvent VOC emissions from insecticide application in ozone nonattainment areas were approximated at 1.5 million pounds (750 tons), or 2 percent of the nationwide combined solvent VOC emissions.

Herbicide usage and herbicide-related VOC solvent emissions were calculated for nationwide use and for herbicide use in ozone nonattainment areas. These results are presented in Tables 4-4 and 4-5. The estimated usage and VOC solvent emissions in Tables 4-4 and 4-5 are only for the years 1987-1989 because this represents the time period of the RFF data base (see Section 4.1.2). The estimated maximum herbicide usage nationwide are 424 million pounds (212,000 tons), or 83 percent of the nationwide combined estimated herbicide and insecticide usage. The estimated solvent VOC emissions from herbicide use nationwide are 86 million pounds (43,100 tons), or 93 percent of the nationwide combined solvent emissions. The estimated maximum AI usage from herbicides in ozone nonattainment areas is 52 million pounds (26,000 tons), or 12 percent of the combined estimated maximum herbicide AI usage nationwide. The estimated solvent VOC

TABLE 4-4. NATIONWIDE SOLVENT VOC EMISSION ESTIMATES FOR HERBICIDE FORMULATIONS

Active ingredient	Pounds AI used <sup>a</sup>	Notes and formulation designation (EC and L)	Fraction AI in nonaqueous solvent formulation <sup>b</sup>	AI pounds in nonaqueous solvent formulation <sup>c</sup>	Formulation nonaqueous solvent fraction <sup>b</sup>	Solvent VOC emissions estimates, pounds <sup>d</sup>
Alazine	68,232,121		0.00	0	0.00	
Alachlor	55,025,302	e	0.41	22,560,374	0.56	28,713,203
Metolachlor	49,544,375	e	0.75	37,158,281	0.10	4,128,698
EPTC	37,119,783	EC <sup>f</sup>	1.00	37,119,783		
2,4-D	33,074,201	L	0.40	13,229,680	0.50	13,229,680
Trifluralin	27,005,509	L <sup>f</sup>				
Cyanazine	22,847,387		0.00	0		
Butylate	19,070,536	EC <sup>e</sup>	0.45	8,581,741	0.14	1,397,028
Pendimethalin	12,475,522	EC	1.00	12,475,522	0.63	20,881,489
Glyphosate	11,535,166		0.00	0		
Decamba	11,254,300		0.00	0		
Bentazon	8,190,359		0.00	0	0.00	
Propanil	7,487,432	e	0.95	7,113,060	0.63	12,111,427
MSMA	4,968,375		0.00	0		
Metribuzin	4,792,132		0.00	0		
Molinate	4,396,189	EC <sup>g</sup>	0.40	1,758,476		
MCPA	4,332,397	g				
Propachlor	4,313,802	EC	0.50	2,156,901	0.50	2,156,901
Propazine	3,972,392	g		0		
Simazine	3,903,902		0.00	0		
Ethalfuralin	3,506,483	f				
Triallate	3,505,008	L <sup>g</sup>	0.32	1,121,603		
Chloramben	2,989,035		0.00	0		
Picloram	2,933,901	f				
Paraquat	2,825,000	g		0		
Clomazone	2,713,716	g				
Bromoxynil	2,620,914	L	0.70	1,834,640	0.66	3,561,360
Linuron	2,599,149		0.00	0		

TABLE 4-4. (continued)

Active ingredient	Pounds AI used <sup>a</sup>	Notes and formulation designation (EC and L)	Fraction AI in nonaqueous solvent formulation <sup>b</sup>	AI pounds in nonaqueous solvent formulation <sup>c</sup>	Formulation nonaqueous solvent fraction <sup>b</sup>	Solvent VOC emissions estimates, pounds <sup>d</sup>
Fluometuron	2,391,268		0.00	0		
DCPA	2,008,871		0.00	0		
Diuron	1,966,524		0.00	0		
Totals:						
Pounds	423,601,051			145,110,061		86,179,785
Tons	211,801			72,555		43,090

<sup>a</sup>RFF data base (1987-1989).<sup>b</sup>Estimate from manufacturers.<sup>c</sup>Total use multiplied by percent use of nonaqueous solvent formulation.<sup>d</sup>Estimated VOC emissions due to nonaqueous solvent.<sup>e</sup>Percent solvent and/or percent formulation used is the average of a range.<sup>f</sup>Percent solvent and/or permit formulation used are considered confidential business information by the manufacturers.<sup>g</sup>Data are unavailable.

TABLE 4-5. OZONE NONATTAINMENT AREA SOLVENT VOC EMISSION ESTIMATES  
FOR HERBICIDE FORMULATIONS

Active ingredient	Pounds AI used <sup>a</sup>	Notes and formulation designation (EC and L)	Fraction AI in nonaqueous solvent formulation <sup>b</sup>	AI pounds in nonaqueous solvent formulation <sup>c</sup>	Formulation nonaqueous solvent fraction <sup>b</sup>	Solvent VOC emissions estimates, pounds <sup>d</sup>
Atrazine	9,630,754		0.00	0	0.00	
Metolachlor	7,398,163	L <sup>e</sup>	0.75	5,548,622	0.10	616,514
Alachlor	5,967,411	L <sup>e</sup>	0.41	2,446,639	0.56	3,113,904
EPTC	2,896,725	EC <sup>g</sup>	1.00	2,896,725		
Cyanazine	2,688,130		0.00	0		
Butylate	2,333,538	EC <sup>e</sup>	0.45	1,050,092	0.14	170,945
Glyphosate	2,223,640		0.00	0		
2,4-D	1,952,924	L	0.40	78,170	0.50	781,180
Trifluralin	1,665,625	L <sup>f</sup>				
Pendimethalin	1,439,202	EC	1.00	1,439,202	0.63	2,408,932
Molinate	1,289,449	EC <sup>g</sup>	0.40	515,780		
DCPA	1,289,430		0.00	0		
Simazine	1,221,504		0.00	0		
Paraquat	992,326	g				
Asulan	893,030	g				
Oryzalin	842,561	g				
Chloramben	766,220		0.00	0		
Linuron	750,603		0.00	0		
Metribuzin	723,406		0.00	0		
Dicamba	709,061		0.00	0		
Bentazon	692,275		0.00	0		
Propanil	626,907	EC <sup>e</sup>	0.95	595,562	0.63	1,014,064
Diuron	542,325		0.00	0		
Oxyfluorfen	462,086	g				
Napropamide	450,935	g				
MCPA	441,538	g				
Thiobencarb	432,190	g				

TABLE 4-5. (continued)

Active ingredient	Pounds AI used <sup>a</sup>	Notes and formulation designation (EC and L)	Fraction AI in nonaqueous solvent formulation <sup>b</sup>	AI pounds in nonaqueous solvent formulation <sup>c</sup>	Formulation nonaqueous solvent fraction <sup>b</sup>	Solvent VOC emissions estimates, pounds <sup>d</sup>
Diphenamid	363,813	g				
Totals:	51,685,771			15,273,791		8,105,528
Pounds	25,843			7,637		4,053
Tons						

<sup>a</sup>RFF data base (1987-1989).<sup>b</sup>Estimate from manufacturers.<sup>c</sup>Use multiplied by percent use of nonaqueous solvent formulation.<sup>d</sup>Estimated VOC emissions due to nonaqueous solvent.<sup>e</sup>Percent solvent and/or percent formulation used is the average of a range.<sup>f</sup>Percent solvent and/or permit formulation used are considered confidential business information by the manufacturers.<sup>g</sup>Data are unavailable.



emissions from herbicide use in ozone nonattainment areas are 8.1 million pounds (4,000 tons), or 9 percent of the combined estimated nationwide solvent VOC emissions.

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## 5.0 EMISSION REDUCTION TECHNIQUES

This section presents information on technically viable methods that may be applied to reduce volatile organic compound (VOC) emissions resulting from the application of agricultural pesticides. The information will allow agency personnel and others to identify the advantages, disadvantages, and probable emission reductions associated with implementing these techniques. A total of seven techniques are discussed, and each is presented in the following format: description of the option, benefits and limitations of the technique, and potential emission reduction levels. The techniques may be used singly or in combination to achieve a desired level of VOC emission reduction.

The implementation of the emissions reduction techniques discussed in this section could occur under two different scenarios. One scenario would have the regulatory strategies to implement any of these emission reduction techniques occurring at the State level rather than on a nationwide basis. The number of ozone nonattainment areas, the level of nonattainment, and agricultural practices vary considerably from one State to another. Because of this, the type of emission reduction techniques and the number of techniques to be implemented may be different for each State. Implementation at the State level allows each State to tailor an emission reduction strategy to fulfill the needs of the State. Under Section 24A of the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), each State may regulate the sale or use of any Federally registered pesticide or device in the State, but only if and to the extent that the State regulation does not permit any sale or use already prohibited by FIFRA.

The second scenario would have implementation occur at the nationwide level. In New York State, the Department of Environmental Conservation encountered problems in attempting to reduce or ban the use of selected consumer products. Under a State implementation scenario, similar problems may occur with some of the control options presented in this section. A second potential problem with State implementation is the creation of a complex market for the pesticide producers which could lead to greater impacts on farmers in some States than in others. Because of the complex market and costs due to product development, production, and registration, some producers may choose to drop use labels for minor crops. Implementation of emission reduction techniques at a nationwide level by EPA, possibly by incorporating ozone air quality concerns into the inert policy, could serve to minimize inconsistencies that may arise at the State level.

Section 5.1 presents techniques for reducing VOC emissions by reformulating liquid pesticides containing organic solvents. Sections 5.2 and 5.3 present a reduction in fumigant usage and alternative application methods, respectively. Sections 5.4 and 5.5 discuss the use of microencapsulation techniques and integrated pest management (IPM) practices. Section 5.6 evaluates the use of alternative active ingredients (AI's), and Section 5.7 presents a discussion of the applications of materials known as "weed oils."

## 5.1 REFORMULATION OF LIQUID PESTICIDES

### 5.1.1 Option Description

This technique requires synthetic pesticide manufacturers to reformulate existing emulsifiable concentrates (EC's) and other liquid pesticide formulations containing organic solvents to eliminate or reduce VOC emissions of the inert constituents, primarily the volatile organic solvents. Organic solvent-based liquids and EC's are widely used because they are low cost to the formulator and easy for the farmer to apply in the field. For example, many AI's are soluble only in petroleum solvents. Liquid formulations also penetrate porous material well and may

provide a more uniform coating on leaves, which improves efficacy. Because the EC's are liquids, they are easy to pour and measure for mixing in the field.

Several strategies could be employed to encourage the reformulation of the existing liquid pesticides. One strategy would be to ban all organic solvent-based liquid pesticides by prohibiting distributors from selling and farmers from using noncomplying pesticides in nonattainment areas. In this case, the manufacturers/formulators would have to label products to prohibit usage in the nonattainment areas. Any change in the labeling requirements is under the authority of the EPA Office of Pesticide Programs (OPP); States do not have authority to require label modifications or changes. As stated earlier, a State has the authority under Section 24A of FIFRA to regulate the sale or use of any Federally registered pesticide or device in the State. This, in effect, could be used to ban use of those formulations whose labels allow use in nonattainment areas.

If all of the organic solvent-based formulations could be phased out over a period of time instead of having an immediate ban in nonattainment areas, this would provide time for developing and testing new pesticide formulations and result in the gradual substitution of organic solvent-based liquids, which would minimize the impact on the growers, regulators, and the pesticide industry.

#### 5.1.2 Benefits and Limitations

The pesticide industry is already under considerable pressure to reformulate organic solvent-based pesticides. The OPP inert strategy is currently driving industry to reformulate pesticides containing the inert ingredients on List 1 (inerts of toxicological concern) or remove the product from the market (see Appendix D for lists 1 and 2). Only a very few of the List 1 inerts are still used; essentially all of them have been replaced. In addition, Department of Transportation restrictions regarding the transport of highly flammable chemicals, which include some pesticide inerts, have encouraged manufacturers to reformulate to less flammable inerts. The problem with an

immediate or complete removal of all EC's and other organic solvent-based liquids is that it could have adverse impacts on those crops, livestock, and forests that rely primarily on these liquid pesticides. Considering that there may not be an effective or appropriate substitute for the removed formulation, the impact on the commodity production and the market could be severe. Therefore, the grower may not have another option or an effective way of resolving the problems caused by an immediate removal.

This emission reduction strategy avoids addressing AI's. Reformulating a pesticide is less costly and time consuming than developing an entirely new AI, which can be a long and costly process. All reformulations must be approved by OPP. Massive reformulations under an air regulation could add years to the process. Changes in the labeling process require an up-front interagency coordination and may also slow down the overall registration process. For individual States, Section 24 of FIFRA may be used to control or restrict the use of a pesticide formulation within that State.

#### 5.1.3 Emission Reduction Potential

The solvent contribution of those pesticides formulated as organic solvent-based liquid pesticides in Tables 4-2 and 4-4 is about 46,400 tons per year.

Current OPP policy is to phase out the solvents on List 1 of the inert ingredients in the pesticide products (see Appendix D). The List 1 compounds are those of toxicological concern and include many of the more common organic solvents that could be used in liquid pesticides, such as the chlorinated hydrocarbons, hexane, dioxane, and others. Inerts on List 1 currently being used as solvents could be eliminated or restricted based on the outcome of the hearings conducted under FIFRA Section 6(6)(2). Current estimates are that those inert compounds presently on List 1 will be replaced or suspended in about 2 years. However, common solvents for liquid pesticide formulations, such as xylene, toluene, and 1,1,1-trichloroethane, are on List 2 (Potentially Toxic Inerts) and could be used in alternate solvent

systems. List 2 inerts are being reviewed and reevaluated by OPP and a number of the compounds currently on List 2 could be promoted to List 1. A few of the current List 2 inerts may be downgraded to List 4 (Inerts of Minimal Concern). Those inerts upgraded from List 2 to List 1 could be replaced or suspended sometime in the future. Therefore, the current OPP policy to eliminate List 1 inerts from registered products will result in little, if any, reduction in the organic solvent contribution to liquid pesticides because alternative solvents are available from List 2.

## 5.2 REDUCED FUMIGANT USAGE

### 5.2.1 Option Description

One option would restrict the volume of sales and the type of application of all or selected fumigants on a State basis under Section 24 of FIFRA. Most fumigants are used in some form of controlled environment so the use and emissions of these chemicals may be monitored. For selected commodities, fumigation chambers are used and the emissions from the chambers can be controlled. Monitoring the use of these chemicals in many agricultural fields should be fairly easy because the application procedure, which uses large plastic sheets to cover the affected area for days or weeks, is so visible. A major use of fumigants is to control the spread of fungi and to reduce destruction of the crop (e.g., grains, corn) by insects and rodents during crop storage.

A second option would be a complete ban on fumigant usage and substitution of liquid or granular products to control nematodes and fungi. Other methods, such as crop rotation and biological means, are also options. Since the restriction on 1,3-dichloropropene, county agents state that many or all of these options have been attempted by farmers in California with varying degrees of success. The overall consensus of the agents from four selected counties was that while substitutes were available, there were efficacy or application problems with each one and acceptable alternatives to some fumigants are not always



available. The fumigants being used as a replacement for 1,3-dichloropropene are discussed in Section 5.2.2.

#### 5.2.2 Benefits and Limitations

Because of the limited number of products affected, a restriction on the total quantity sold and the specific application for the fumigants may be easier to implement than a total ban. Since the use of fumigants is not totally banned, but restricted, there may not be any adverse impacts on the growers who have to use fumigation.

Currently, no substitutes are available in the market and the impacts of the options must carefully be studied for each of the fumigants. The use of one of the key fumigants, 1,3-dichloropropene (Telone®), is suspended in California pending the outcome of testing to respond to air toxics concerns. In addition, OPP's Special Review and Reregistration Division also has this fumigant under special review, but the results are unknown at this time. In California, alternative fumigants being used during the suspension of 1,3-dichloropropene include Metam-sodium, methyl bromide, and Nemacur®. Although each of these pesticides can be substituted for 1,3-dichloropropene in selected applications, each of these has its own problems or limitations.<sup>1</sup> In addition, the issue of substitution concerning each of these alternatives is very crop-specific.

Metam-sodium is formulated as a concentrated solution and is stable so long as the solution remains concentrated. During application, the concentrated solution is applied to the field and the field watered. The AI is unstable in dilute solution, and watering the field after application dilutes the concentrated solution, resulting in hydrolytic decomposition of Metam-sodium. The decomposition product(s) volatilizes and acts as the actual fumigant. The major problems with this AI lie with handling the concentrated solution and the resulting decomposition if the solution is accidentally diluted.

Methyl bromide is a gas and must be handled in pressurized containers. This AI is toxic to humans, and the potential

problems lie with handling pressurized tanks during shipment and application.

Nemacur® is formulated either as an EC or a granular and, in Section 5.1, the emission reduction option is the reduction or elimination of EC formulations. Currently, the AI is applied by broadcast, in-the-row, in bands, and by drench methods.

#### 5.2.3 Emission Reduction Potential

Fumigants could represent a large emission reduction potential from a single class of synthetic pesticides depending upon the application of the fumigant. Based on the data in Table 4-2 for dibromochloropropane (DBCP) and ethylene dibromide (EDB), the total quantity used is approximately 21,000 tons/yr. Although the use of DBCP was discontinued in 1987 and EDB is not registered for agricultural use in the United States, it has been assumed that an equal quantity of substitute fumigant has replaced DBCP and EDB.

In California, 1,3-dichloropropene accounted for a large volume fumigant usage until its use was suspended in April 1990. The three fumigants being used as replacements for the suspended fumigant provide varying potential for emission reductions. Metam-sodium is commonly applied to a field as a concentrated solution and then diluted with water which results in hydrolysis to form a volatile product. For this application, little or no potential for emission reduction exists. This fumigant can be used as a solid for selected applications (e.g., as a nematicide). Although the potential for emission reduction is significant, the quantity used for this application is small. Methyl bromide is a gas so no potential for emission reduction exists for this fumigant. Nemacur® is formulated as a granular product and a potential for emission reduction is present.

The estimated maximum reduction potential is difficult to predict because of specific application requirements. If solid formulations can be used for field applications, the overall potential for emission reduction could be significant because of the much lower vapor pressure of solid formulations and also because of incorporation into the soil. For crop storage in

elevators or bins, a gas or volatile liquid product is the most effective treatment method to obtain good mixing between the crop and the fumigant. Use of these products would present very little potential for emission reduction.

### 5.3 ALTERNATIVE APPLICATION METHODS

#### 5.3.1 Option Description

This option would require the application equipment manufacturer to develop and demonstrate improved-efficiency application equipment. Current research from a limited study in California on strawberry plants has resulted in promising information on equipment to improve application efficiency.<sup>2</sup> The study, conducted at the University of California-Davis, determined pest control efficacy achieved by reduced-volume sprays of charged and uncharged droplets delivered to the plants in air-carried jets. In early season trials, the reduced-volume applications and the conventional high-volume applications appeared to control mites equally well. Deposition studies showed the reduced-volume equipment deposited slightly higher amounts of pesticide on the leaf, with more persistent deposition. Deposition studies conducted in July/August showed the reduced-volume, charged sprayer achieved about 32 percent greater deposition and 36 percent greater half-life than a conventional application at the same AI amount per acre. Using the reduced-volume sprayer, applying the AI at 50 percent of the rate of a conventional sprayer gave almost the same deposition quantity and half-life.

Soil incorporation during application can be an effective method to reduce pesticide volatilization. Data in Table 4-1 showed this method significantly reduced the percentage of pesticide lost compared to application by surface spraying.

An operator training program could be required in conjunction with the sale of the improved-efficiency application system and could be included as part of a Statewide licensing program.

### 5.3.2 Benefits and Limitations

Although the results of the reduced-volume sprayer study are only for one type of crop using one alternative system, the results indicate improvements in overall pesticide application efficiency are possible. If equal improvements can be shown for other systems, improved application efficiencies may result in reduced pesticide application quantities of up to 30 to 50 percent.<sup>3</sup>

Improving application efficiency may significantly reduce worker exposure and drift-related problems. The industry is already under considerable pressure to reduce these types of exposure, and an air regulation will be consistent with programs that are currently underway, such as drift-reduction training.

Purchasing new application equipment or parts could place a significant economic burden on individual farmers or commercial applicators. The cost impact of the new equipment would depend upon the type of equipment or the required parts. By phasing in the regulation, the financial burden may be reduced significantly and result in a considerably more receptive atmosphere for the new regulation by the farmers and commercial applicators.

Revising application methods may result in formulation changes, which may have emissions or other environmental impacts.

Important variables such as applicator training and experience, weather conditions, equipment maintenance and calibration practices, and formulation of the pesticide all affect efficiency, and therefore need to be carefully considered.

### 5.3.3 Emission Reduction Potential

No information was found to identify those active ingredients that could be applied with reduced-volume application equipment. Therefore, there are no data to suggest that this method would not be applicable to all liquid pesticide formulations. If the results of the study at the University of California-Davis are indicative of the reduction in application rates that could be achieved, it is possible that new equipment could result in an application rate one-half of the current rate for a conventional spray applicator.

## 5.4 MICROENCAPSULATION

### 5.4.1 Option Description<sup>4,5</sup>

This strategy would require pesticide manufacturers to develop microcapsule formulations for all AI's currently formulated as an EC or an organic solvent-based liquid or demonstrate that this type of formulation is not technically feasible for a specific AI.

Microencapsulation is a process whereby very small particles or droplets are encased by a coating, usually polymeric, to produce very small capsules. In simple terms, a microcapsule is a small sphere with a uniform wall surrounding it. The material inside the microcapsule is referred to as the core, internal phase, or fill and the wall is called the shell, coating, or membrane. For pesticides, the principal component of the core is the specific AI; a small amount of solvent is also present in the core. Most microcapsules are envisioned to be small spheres having diameters in the range of a few micrometers to a few millimeters. However, many microcapsules have shapes considerably different from spheres because the core may be a crystal, a jagged sorbent particle, a suspension of solids, an emulsion, or a suspension of smaller microcapsules. The final microcapsule may even have multiple walls.

In forming microcapsules for a pesticide AI, the basic process is the formation of a plastic shell around a droplet containing the AI. This process is carried out in an emulsion. Many techniques are available to produce microcapsules but the most common process for pesticide AI's is the chemical method of interfacial polymerization. In this method, under the proper conditions, two reactants in a polycondensation meet at an interface and react rapidly to form thin flexible walls. For pesticide AI's, two monomers are selected that will react to form the microcapsule. One of the monomers is water-soluble and the other is insoluble in water. The selection of the specific monomers depends upon the solubility of the AI, the ultimate use of the formulation, and the particular properties required of the microcapsules. The pesticide AI is dissolved in one of the

monomers, and this solution is combined with a solution of the second monomer to form an emulsion. The microcapsules are formed from this emulsion by interfacial polycondensation.

There are primarily three processes for forming microcapsules, two patented processes based on the chemical method of the interfacial polycondensation and the third on coacervation. The process patented by Monsanto produces the highest concentration of AI (4 pounds [lb] of AI per gallon [gal] of solution). In the patented Pennwalt process, the maximum concentration of AI is approximately 2 lb/gal. Formation of microcapsules by coacervation, the third process, results in the formation of very dilute concentrations of AI.

#### 5.4.2 Benefits and Limitations

Microencapsulating a pesticide AI can be a very effective method to reduce the quantity of solvent compared to EC's or organic solvent-based liquids and to control the rate of release of the AI and volatile constituents of the formulation into the environment. The primary benefit of this method is the reduction in the quantity of solvent.<sup>5</sup> The reduced rate of release of the components from the microcapsule does not necessarily correspond to an additional reduction in VOC emissions. The slower release rate only extends the quantity emitted over a longer period of time unless it can be assumed that during that time hydrolysis and microbial degradation will destroy a portion of the VOC's. If this destruction occurs, a limited reduction in VOC emissions could be anticipated. Monsanto originally developed the microencapsulation process for alachlor because of groundwater contamination problems associated with using EC formulations of the AI.

Microcapsules can be produced at a size equivalent to a grain of very fine sand or smaller. These microcapsules can be suspended in water and applied to the target crops using ordinary liquid spray equipment. Purchase of special spray equipment is not required.

Microencapsulation is not a universal answer to reduced organic solvent usage and the emission of VOC's from pesticide

formulations. For some AI's, it is very difficult to form a stable emulsion, which is necessary to produce the microcapsules.

A potential major production problem associated with microencapsulation is the absence of any method to recover the AI from a bad formulation. In many other processes, if a problem occurs during formulation and the final product does not meet specifications, adjustments can be made to the formulation to bring the product within specifications and the AI is not lost. In microencapsulation, if a problem occurs during production of the microcapsules, there is no way to recover the AI and the entire batch is lost. Thus, microencapsulation can be an expensive production method unless it is used only with AI's that will allow the formation of very stable emulsion systems.

The formation of microcapsules with high AI concentrations (i.e., 4 lb AI/gal) makes the product more economical to manufacture. However, the patents for producing microcapsules at this concentration are held by Monsanto and are not generally available. These patents expire in July 1998. As the concentration of the AI decreases, the product becomes less economical to manufacture.

Subsequent to field application, microcapsules can present a potential hazard to honey bees and other pollinators.

#### 5.4.3 Emission Reduction Potential

The solvent contribution of all EC's and organic solvent-based liquid formulations in Tables 4-2 and 4-4 is about 46,400 tons/yr. It cannot be anticipated that all of these formulations could be converted to microencapsulation, and the actual number of AI's that could be reformulated and used as microcapsules is not known.

### 5.5 INTEGRATED PEST MANAGEMENT

#### 5.5.1 Option Description

Integrated pest management (IPM) is an ecologically based pest management program that combines biological and nonbiological control techniques to suppress weeds, insects, and diseases. This option has been defined as a pest population management system that utilizes all suitable techniques in a

compatible manner to reduce pest populations and maintain them at levels below those causing economic injury. The IPM approach has been used in varying degrees for 20 years and, in some instances, may reduce the effects of pesticides on groundwater, soil, and wildlife.<sup>6</sup> This pest management program encompasses a variety of farming practices including:

1. The use of naturally-occurring agents, such as predator insects and biological agents;
2. Increased crop rotation and tillage in areas where erosion is not an overriding factor;
3. Removal of crop refuse, close timing of planting dates, and selection of optimal planting sites;
4. Careful management of water and fertilizer use; and
5. As appropriate, reduced and controlled pesticide use.

The IPM system encourages the coordinated use of a variety of practices that are generally familiar to farmers.

Current IPM programs address the potential adverse health and environmental effects that can result from instances of excessive pesticide use. They also consider the decreased effectiveness of some of the chemical pesticides because some pests and plants have developed an increased resistance to these substances. Integrated pest management customizes the use of a variety of pest suppression techniques to selected individual circumstances; IPM applies pesticides sparingly and only when dictated by economic conditions. In the correct situation, IPM has played and can continue to play a significant role in reducing pesticide exposure to humans, contamination of the environment, and potential threats to endangered species. This can be accomplished while providing economic advantages to the farmer. However, it should be recognized that IPM is not currently successful in all situations. Each potential use of the IPM concept should be evaluated on an individual basis.

The key word in all IPM programs is integration. Farmers should consider all of the pest control methods available to them to provide for the most effective use of pesticides. For example, in some instances introduction of biological enemies of



pests may prove to be a desirable alternative to the use of certain pesticides. Because IPM systems can be customized to address specific problems, they can accommodate a wide range of agricultural and environmental needs.

#### 5.5.2 Benefits and Limitations

The benefits from the IPM system vary with the circumstances under which the system is used. Virtually all farmers, regardless of the size of their enterprises, can benefit to some degree from using this system. The principal benefits can be a reduction in expenditures for pesticides, reduced economic risk associated with rotating crop production versus single-crop production, and maintenance of crop yield at essentially the same levels.

Limitations of using the IPM system could include some combination of reduced pest eradication efficiency, undesirable environmental side-effects (e.g., increased soil erosion), increased operating costs, difficulties in enforcement by State agencies, and resistance to changes to long-established farming policies within a realistic time frame. In addition, some IPM opponents state that changes to current farming practices would reduce the quality of the product, reduce crop yield, and result in higher food prices.

#### 5.5.3 Emission Reduction Potential

The overall reduction in VOC emissions attributable to the accelerated incorporation of the IPM systems is difficult to estimate. A study in 1977 stated that IPM may show a reduction in pesticide usage as high as 33 percent to 67 percent.<sup>7</sup> The reduction in VOC emissions is a result of reduced use of EC's and organic solvent-based liquid formulations. It is not known whether the 33 to 67 percent reduction in usage would also apply to these two formulations or whether reductions this high can be achieved for other crops in different locations. :

### 5.6 REDUCED USAGE OF SELECTED PESTICIDE AI'S

#### 5.6.1 Option Description

A use-reduction plan for specific pesticide AI's could also be instituted to reduce VOC emissions. The targeted pesticides

may be AI's for which lower-VOC AI substitutes are readily available (or which could be developed) or for which the use of the AI at current levels is considered optional or marginal. This type of regulation is more compatible with the current OPP policy of evaluation on an AI basis.

#### 5.6.2 Benefits and Limitations

The regulation could be integrated with current State regulations and programs, such as a required license to apply pesticides, or by a pesticide usage report, such as the one required by the State of California. It could also be implemented using Section 24 of FIFRA.

The data base used to select targeted AI's and emission-reduction targets must be current because significant changes in use patterns from year to year could reduce or negate the potential emissions reduction. It would obviously be futile to reduce or consider an AI that is no longer used at high levels because use patterns have changed.

The targeted list must be constantly updated and reviewed to ensure that the regulation is obtaining the desired emission reduction. The potential benefit may be easily undermined by increases in emissions from nonregulated pesticides. Some of the alternative formulations may have equal or greater VOC impact than the current EC formulations if an increase in volume usage occurs. Because the AI's are volatile, VOC emissions from the alternative pesticides may increase despite the lack of inert solvent. This increase would occur if the efficacy of the AI is decreased as a result of the formulation, requiring a greater application rate. The less volatile solvents are also generally poorer solvents. Therefore, a less concentrated formulation may result and a higher application rate may be required to apply the same quantity of AI.

One of the major limitations to this option is the potential necessity for developing a new AI if an existing alternative AI is not available. The development of a new AI can take years with no assurance that the new AI can be competitive in terms of efficacy, formulation type, or cost. After the manufacturer has

decided to register the new AI, the FIFRA registration process can take 3 or more years and the cost of a complete registration can range from \$50 million to \$70 million (see Section 7.1).

## 5.7 REDUCED USAGE OF CROP OILS

### 5.7.1 Option Description

Crop oils and weed oils are defined as petroleum-based products used as herbicides, carriers for synthetic herbicides, or insecticides. Crop oils, used for controlling insects and mites, are highly refined products that have to be registered with EPA. Oils used for the indiscriminate destruction of vegetation do not have to be registered. The most common usage of crop oils is as insecticides; usage as herbicides and carriers for herbicides is very limited. A major manufacturer of a synthetic herbicide indicated that some weed oils, such as Stoddard solvent for weed control, were used for many years but the use of these products has decreased to a low level and they are not considered as competition for the synthetic herbicides.<sup>8</sup> For usage as a carrier for herbicides, the formulated product often contained 1 to 1.5 percent AI, 1.2 to 1.5 percent crop oil, and the remainder as organic solvent.

Typically, crop oils are used as insecticides. The oils are paraffinic and highly refined with unsulfonated residues in excess of 92 percent. The higher the percentage of unsulfonated residues, the less toxic or harmful the oil is to the plants to which it is being applied. Application of the crop oil is designed to kill the insects but allow the plant to remain unharmed. Action of the crop oils as insecticides is through suffocation of the insects. For dormant application, the oil is usually applied at a concentration of 3 to 4 percent oil in water. For summer application, a concentration of about 2 percent oil in water is used. The cost of insecticidal oils varies considerably but is usually determined by the labeling of the products, location of the purchase, and other market factors. Crop oils for summer application typically are more expensive than dormant oils.

### 5.7.2 Benefits and Limitations

Synthetic substitutes have a lower VOC-emitting potential because they tend to be applied at lower rates.

The use of crop oils in California is decreasing, and some of the major suppliers are leaving the market because of the cost of meeting registration requirements.

The manufacturers of crop oils are not major pesticide manufacturers, so they may be slightly affected by the reduction because these products are a small portion of their overall business.

Some crop oils can be used in organic farming and are an integral part of IPM programs. Restricting the use of these products could discourage farmers from using these programs, which are perceived to have other significant environmental and safety benefits. In addition, insecticide oils would likely have to be replaced by one or more applications of other insecticides.

### 5.7.3 Emission Reduction Potential

The total quantity of crop oils used on a nationwide basis is unknown. Because these products are not registered AI's, they were not included in the Resources for the Future (RFF) data base. Data obtained from the California Air Resources Board (CARB) showed an estimated 1987 usage of 18,600 tons/yr.<sup>9</sup> Draft preliminary data from California has an estimated 1990 usage for crop oils at 13,615 tons.<sup>10</sup>

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## 6.0 ENVIRONMENTAL ANALYSIS

This section discusses the environmental impacts associated with implementing the various emission reduction alternatives discussed in Section 5.0. The primary emphasis is on a quantitative assessment of the impacts on air quality by volatile organic compound (VOC) emissions as described in Section 4.0 and after implementation of the control alternatives. The impacts of these control alternatives on water quality, solid waste, energy, and biota are also briefly discussed in this section.

### 6.1 AIR POLLUTION

The estimated percentage solvent VOC emission reductions for each reduction technique nationwide and in ozone nonattainment areas are presented in Table 6-1.

Although each of the reduction techniques is presented separately, some could be implemented together to further reduce emissions from this source. For example, emulsifiable concentrates (EC's) can be reformulated to contain less organic solvent at the same time that fumigant usage is reduced.

Implementing any of these reduction techniques would reduce VOC emissions from pesticide application. However, the reduction potentials as calculated are not additive in all cases because they may apply to the same VOC emissions. For example, addition of the emission reductions due to reformulation of 100 percent of an EC to a granule and reformulation of 50 percent of the same EC to a microencapsulated formulation overestimates the solvent VOC emission reduction.

#### 6.1.1 Reformulation

Tables 4-2 and 4-4 list the nationwide solvent VOC emissions from EC's and organic solvent formulations. Tables 4-3 and 4-5

TABLE 6-1. SUMMARY OF ESTIMATED SOLVENT VOC EMISSION REDUCTIONS

Emission reduction techniques	Notes	Formulation component	VOC emissions due to solvent, tons <sup>a</sup>		Estimated achievable reduction of target, percent <sup>b</sup>
			Nationwide	Nonattainment	
Reformulation	c	Solvent	46,400	4,800	≤100
Fumigants	d	Fumigants	20,700	4,750	≤100
Application efficiency	c	Solvent	46,400	4,800	≤30
Microencapsulation	c	Solvent	46,400	4,800	≤100
IPM	c	Solvent	46,400	4,800	≤33

<sup>a</sup>Maximum emissions due to solvent from Tables 4-2 through 4-5.

<sup>b</sup>Percent reduction estimates discussed in Chapter 5.

<sup>c</sup>Target is due to solvent emissions from Tables 4-2 through 4-5.

<sup>d</sup>Target emissions are fumigant (ethylene dibromide and dibromochloropropane) use from Tables 4-2 and 4-3.

list the solvent VOC emissions in ozone nonattainment areas. The reductions achieved by this reduction technique were assumed to affect solvent content only and reflect no decrease in potential AI VOC emissions. The maximum solvent VOC emission reductions due to implementing this technique are 46,400 tons nationwide and 4,800 tons in ozone nonattainment areas.

#### 6.1.2 Example of Reduced Fumigant Usage

The VOC emission reduction potential due to reducing fumigant usage is assumed to be 100 percent of the contribution due to dibromochloropropane (DBCP) and ethylene dibromide (EDB). The nationwide and ozone nonattainment area contributions due to these two fumigants in 1982-1984 are listed in Tables 4-2 and 4-3, respectively. The reduction indicated in Table 6-1 has already taken effect due to the cancellation of agricultural use registrations for EDB and DBCP. Usage data on other currently used fumigants such as Telone®, metam, methyl bromide, and chloropicrin were not available to calculate emission reductions. The estimated maximum VOC emission reductions due to removing EDB and DBCP are 20,700 tons nationwide and 4,750 tons in ozone nonattainment areas.

#### 6.1.3 Use of Alternative Application Methods

The reduction potential from using alternative application methods was calculated for all solvents listed in Tables 4-2 through 4-5. A reduction factor of less than or equal to 30 percent (see the discussion in Section 5.3.2) can be used to estimate the maximum solvent VOC emissions. The maximum solvent VOC emission reductions due to implementing increased efficiency application methods are estimated to be less than or equal to 14,000 tons nationwide and less than or equal to 1,400 tons in ozone nonattainment areas.

#### 6.1.4 Increased Use of Microencapsulated Pesticides

The reduction potential from increased use of microencapsulated pesticides was calculated in the same manner as reformulation, by estimating the effects of reformulating EC's and organic solvent-containing AI formulations. The solvent VOC emissions due to these AI's was subtracted from the maximum VOC



emissions estimate. However, since 100 percent reformulation of EC's and organic solvent-containing formulations into microcapsules is not likely due to various formulation constraints, a factor of less than 100 percent should be applied to the solvent VOC contribution of this target to calculate the VOC reduction. The reductions achieved by this alternative were assumed to reflect no decrease any in potential AI VOC emissions. Table 6-1 presents the reduction potential for this technique. The maximum solvent VOC emission reduction due to implementing this technique are less than or equal to 46,400 tons nationwide and less than or equal to 4,800 tons in ozone nonattainment areas.

#### 6.1.5 Integrated Pest Management

The solvent VOC reduction potential of integrated pest management (IPM) was calculated from the solvent VOC contribution due to all pesticide applications from Tables 4-2 through 4-5. The percent reduction for this technique is a factor of less than or equal to 33 percent as discussed in Section 5.5.3. The maximum solvent VOC emission reduction due to implementing IPM are estimated to be less than or equal to 15,300 tons nationwide and less than or equal to 1,600 tons in ozone nonattainment areas.

#### 6.1.6 Crop Oils

No VOC reductions could be calculated for the use of crop oils due to insufficient information on reduction techniques.

#### 6.1.7 Active Ingredients

The emission reduction estimates ascribed to two control techniques, application efficiency and IPM, can also be applied to VOC emissions due to active ingredients. For each of these two control techniques, the potential for the reduction in emission decreases as the overall potential for emissions is reduced.

### 6.2 WATER POLLUTION

Implementing any of these control technologies would result in no adverse water pollution impacts because no hazardous

wastewater is produced by applicators correctly using these alternatives.

#### 6.2.1 Surface Water

The impact on surface water bodies from pesticide runoff may be affected by a change in pesticide formulation. Subsequent to the field application of those AI's dissolved in organic solvents (i.e., EC's), these formulations could be susceptible to rapid runoff during rain because the EC is not strongly sorbed to soil particles. During the rain, an emulsion could be formed with the rainwater to facilitate the runoff. As the organic solvent in the EC volatilizes, the AI remains on the soil surface where it can be more readily sorbed to the soil particles. Reformulation of the EC's could result in products that would be less susceptible to runoff than the liquid EC and could lead to greater availability of the AI to be sorbed to the soil. In general, water-insoluble AI's are more likely to be found in sediments than in the water column of surface waters.

Improved application efficiencies or the use of IPM may, in many instances, result in the overall reduced usage of AI's and a net reduction in total surface water concentrations.

#### 6.2.2 Groundwater

The impact on groundwater of water-insoluble AI's also varies with the formulation of the pesticide. An EC may be dissolved in the groundwater and be transported with the groundwater flow.

Reformulation of the EC's to remove the organic solvents that form an emulsion in water decreases the aqueous solubility of the AI. The AI may be sorbed to soil particles or move through the unsaturated zone above the groundwater. Rain may wash the AI as a particle or as a droplet down into the groundwater where it will be suspended if not soluble and be transported with the groundwater flow. However, as described in detail in Section 3.3.7.2, soil moisture content also affects evaporation of the AI. An increase in soil moisture increases the evaporation rate of the AI.

Many of the other potential VOC control strategies may lead to an overall reduction in the quantity of AI used or better application efficiency resulting in greater AI utility by the plant. The impact of these strategies is a further overall reduction in the availability of the AI's to the soil and therefore reduced potential for groundwater contamination.

The impacts of pesticides on groundwater are not quantitated here. However, it has already been assumed that evaporation of pesticides to the atmosphere is the most likely fate of applied pesticides, even though there are possible groundwater contamination pathways. Contaminated groundwater in aquifers used for drinking water supplies can seriously impact human health. The Environmental Protection Agency (EPA) completed in 1990 a 5-year National Survey of Pesticides in Drinking Water Wells (NPS). A summary of the final results of this survey was published in the fall of 1990 and the complete Phase I report was published in 1991. Between 1988 and 1990, EPA sampled approximately 1,300 community water system (CWS) wells and rural and domestic wells for the presence of 101 pesticides, 25 pesticide degradates, and nitrate.<sup>2</sup> Pesticides and pesticide degradates were detected much less frequently than nitrate. The two pesticides most frequently detected were DCPA acid metabolites and atrazine. Ten other pesticides were detected above Survey reporting limits: DBCP, dinoseb, hexachlorobenzene, prometon, simazine, alachlor, bentazon, EDB, ethylene thiourea, and lindane. Of those pesticides with Lifetime Health Advisory Limits (HAL's), EPA estimates that at most 750 CWS wells and 60,900 rural domestic wells nationally have at least one pesticide above its respective HAL.<sup>2</sup>

### 6.3 SOLID WASTE DISPOSAL

The increased quantity of solid waste generated by implementing these technologies is unknown but believed to be insignificant. No apparent new application related waste streams would be generated from any of the alternatives.

#### 6.4 ENERGY .

Implementing these control technologies would change energy consumption related to a change in the manufacturing process of a different pesticide formulation. The potential energy consumption increase or decrease is unknown and would be highly specific to the manufacturer. The difference in energy requirements for applying various pesticide formulations is believed to be insignificant.

#### 6.5 BIOTA

In general, the formulation of a pesticide influences its exposure, and therefore toxicity, to nontarget species. The effects of formulation on toxicity are most apparent in aquatic ecosystems. For fish, insecticide emulsions and oil solutions are the most toxic types of formulations.<sup>3,4</sup> Emulsifiable oil preparations of benzene hexachloride were 25 times more toxic to golden shiners than wettable powder formulations containing the same level of gamma isomer.<sup>3</sup> Solvents may also contribute to the toxic effects and absorption of pesticides by aquatic species.<sup>4,5</sup> Granular formulations, wettable powders, and dusts, which usually release the AI's into the aquatic ecosystem at slow rate, have relatively low toxicities to fish.<sup>6</sup> Pesticides that accumulate in surface water sediments, if persistent, can impact benthic organisms which are an important part of aquatic ecosystem food chains. The entire ecosystem will be affected by changes in the benthic community. Granular formulations are under study by the Office of Pesticide Programs for adverse effects on birds. Birds have been found to consume granular pesticides after application to the crop, which may result in increased avian mortality. Studies of subsurface application of granular formulations have shown promise for a partial reduction in bird exposure. Comprehensive studies on ecosystem effects due to pesticide formulations were not found in the literature or through contacts with agricultural research centers.<sup>7,8</sup>



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## 7.0 CONTROL COST IMPACTS

This section discusses the range of control cost impacts associated with implementing the control alternatives discussed in Section 5.0. The majority of information is related to costs of reformulating active ingredients (AI's), Federal and State registration costs, and costs of banning fumigants. The cost impacts of alternative application methods and integrated pest management (IPM) are also briefly discussed in this section.

### 7.1 REFORMULATION

In general, there are several areas to consider when identifying the individual costs associated with changing the formulation of an AI. Manufacturing and packaging processes may need to be changed, depending on the nature of the new formulation. Registration of the new product is required under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Manufacturers are required to conduct various studies in order to collect data on the pesticide product in support of its registration. The number of studies required and, therefore, the overall cost is related to a number of factors, which are discussed below. Registration fees on the Federal and State-levels are also required. Consumers of the new pesticide product may be required to purchase new application equipment to accommodate the new formulation. Consumers will also be affected by increased prices from increases in manufacturing costs, if any. Information is presented below on cost impacts due to reformulating an AI.



#### 7.1.1 Production Costs

A range or average cost estimate for manufacturing reformulation costs is not available due to the highly variable nature of AI's and a number of manufacturing circumstances.<sup>1,2</sup> The manufacturing process required to reformulate an AI to a formulation other than an emulsifiable concentrate (EC) likely will be more difficult and expensive because EC's are relatively easy to make.<sup>2</sup> Costs to retool the manufacturing process are variable and unknown.<sup>1,2</sup> Major retooling is necessary if the production facility made only EC's and must change completely to accommodate a new process. However, it is reasonable to expect that some large facilities house more than one process and would not require completely new equipment. Thus, a wide range in costs is likely.

Some AI's are currently only formulated as EC's and would be very difficult to reformulate due to chemical or physical properties.<sup>1</sup> However, it is impossible to generalize which pesticide compounds can only be formulated as EC's. The individual properties of compounds (e.g., AI's) vary greatly even within a class of compounds or pesticides (e.g., chlorinated hydrocarbons, organophosphorus, and carbamate compounds, which are classes of AI's).<sup>1</sup> Another consideration is costs added to the manufacturing process due to the new formulation process. For example, formulation processes that result in dust formation (e.g., wettable powders, granules, dusts, baits) require measures to suppress and control the dust during manufacturing and packaging.<sup>2</sup>

#### 7.1.2 Registration Costs

All pesticide products must be registered for sale or distribution under FIFRA. It must be emphasized that a pesticide formulation cannot be arbitrarily changed without the occurrence of significant other impacts. Reformulation of an AI may be considered minor or major depending on the nature of the changes made. The determination of what constitutes a major or minor change is made on a case-by-case basis by EPA.<sup>3</sup> For example, a minor change may consist of a change in the solvent or percent of

solvent. If the change is minor, an amendment to the registration of the original product may be all that is required.<sup>3</sup>

A new registration is required for a product that has had a major change in its formulation. For example, changing the formulation from an EC to a dust is likely to be considered a major change.<sup>3</sup> The costs to complete a new registration for a pesticide product vary considerably. Total costs obtained from industry sources are presented in Table 7-1.

In addition, State laws and regulations also may apply to the registration of pesticide products. State end-use product registration fees vary from State to State. Not all States require registration fees, but if a new product were to be registered in all States that do require fees, the total cost in the first year of registration would be \$1,425.<sup>7</sup> The State of Iowa increases the fees of a pesticide product after the first year according to the sales of the product. Therefore, the total for State fees could go as high as \$3,000 a year in the following years depending on the volume of sales of the pesticide in Iowa.

Most of the variability in the cost of registering a pesticide product comes from the studies required to provide data to EPA in support of the registration. According to FIFRA, the registrant provides the study results to demonstrate that the pesticide will not cause unreasonable adverse effects on human health or the environment when it is used according to approved label directions. Studies that are generally required are listed in 40 CFR 158, Data Requirements for Registration.

The specific studies that are required or conditionally required are determined by the general use pattern of the product being registered (i.e., food crop use, nonfood crop use, forestry use, domestic use, indoor use, minor crop use, etc.). The studies are designed to provide information on the pesticide product in the following areas: environmental fate, acute and chronic toxicology, reentry protection, spray drift, effect on wildlife and aquatic organisms, nontarget plant protection data, nontarget insect data, and product performance. These studies

TABLE 7-1. SUMMARY OF ESTIMATED COSTS FOR REGISTRATION.<sup>4-8</sup>

Category	Item	Estimated costs, \$
FIFRA registration data collection	Theoretical product reregistration with one crop use, one target insect, one method of application, one use Estimated to take 3 years to complete	110,000
	Actual industry figures--high end of range: one AI (insecticide) with many uses and avian and mesocosm studies required - 1987 data call in - 1988 registration standard	17,100,000 789,000
	Actual industry figures--low end of range: one AI nonfood use product with only one use - to fill data gaps - to replace old studies - probable maximum at completion of registration	1,475,000 1,200,000 5,029,000
	New product estimated cost range for complete registration	50,000,000 to 75,000,000
FIFRA registration fees	Reregistration fee Payable in two installments, may be shared by all manufacturers of the AI	150,000
	New chemical registration review	184,500
	New biochemical and microbial registration review	64,000
	New use pattern registration review	33,800
	Experimental use permit review	4,500
	Old chemical registration review	4,500
State registration fees		1,425

are conducted on the end-use product, technical-grade AI, radio-labeled pure AI, typical end-use product, or manufacturing-use product as specified in Part 158. Estimated costs for all potential studies in these areas are listed in Table 7-2. One estimate of costs consists of those costs provided by the Office of Pesticide Programs (OPP) to the Office of Management and Budget (OMB) in 1991. The other estimates were made in 1991 by a representative of the California Department of Food and Agriculture's Pesticide Registration Branch. All of the studies possible in each of the study areas are not required in every case. Therefore, the costs in Table 7-2 are conservatively high. In cases where the Part 158 studies are not adequate to assess the potential risk of a product, EPA may request additional studies.

Changes to a pesticide formulation that would not alter the potential risks of the pesticide product and, therefore, would not require scientific review by EPA may be considered minor changes by EPA. In the case of a minor change, the registrant may be able to cite existing data to fulfill the data requirements on various properties of the AI and include the results of six acute toxicity studies (listed in Table 7-3) conducted on the end-use product formulation that are required for this type of amended registration.<sup>3</sup> If a new use pattern is requested, efficacy data is required. An amendment to the registration also may be possible for minor changes to the use pattern.

Another type of registration that does not require extensive data collection is called a "me-too" registration. The "me-too" end-use product must be essentially the same as a currently registered product.<sup>3</sup> The ingredients, use patterns, and instructions for application must be the same. The registrant for a "me-too" product must obtain permission from the other registrant to use the registration data developed for the similar product and include a copy of the other products' label. The estimated costs of the acute toxicological studies required are

TABLE 7-2. SUMMARY OF COST ESTIMATES FOR FIFRA STUDY AREAS

Study area	Estimated cost <sup>9</sup> , \$	Estimated cost <sup>10</sup> , \$
Product chemistry	148,400	300,000 to 500,000
Hazard evaluation: wildlife and aquatic organisms	690,000	
Hazard evaluation: humans and domestic animals	2,864,000	2,700,000 to 3,000,000
Plant protection	358,500	
Reentry protection	185,300	
Environmental fate	1,616,500	
Spray drift	28,000	
Residue chemistry		
-general	509,000	--
-per crop	468,500	50,000 to 75,000

TABLE 7-3. SUMMARY OF ESTIMATED COSTS FOR AMENDED OR "ME-TOO" REGISTRATION<sup>9</sup>

Category	Item	Cost, \$
Amended registration data collection	Acute oral tox.-rat	3,900
	Acute dermal tox.- rabbit/rat	6,700
	Acute inhalation tox.-rat	11,100
	Primary eye irritation-rabbit	1,800
	Primary dermal irritation	1,700
	Dermal sensitization	5,600
Registration fees	Amended registration fee	700
	State registration fee	1,425
	Total	32,925

presented in Table 7-3, along with the fees for an amended Federal registration.

The EPA determines which studies are required to register an EC that has been reformulated to a lower solvent content formulation, a microencapsulate reformulated from a solvent-containing formulation, and to add new uses to potential alternatives for fumigants. The extent of the required studies depends on many factors including the characteristics of a given AI and pesticide formulation, whether or not there are formulations similar to the desired formulation currently on the market, and current use patterns of the formulation. Because of this complexity, no estimates of testing requirements for specific formulations can reasonably be made.

## 7.2 APPLICATOR EQUIPMENT COSTS

Consumers apply the pesticide products with a variety of equipment depending on the formulation of the product. An applicator or farmer may own one or more types of application equipment. The equipment used may depend in part on the types of formulations the farmer believes are most effective on the crops treated and the formulations in which desired products are available. The cost of application equipment varies considerably. Table 7-4 presents a summary of the equipment costs gathered from various agricultural equipment companies. Another cost that the consumer may incur due to reformulation of an AI is the increased cost of the new product compared to the original. This price increase is particularly likely for reformulation of EC's due to the inexpensive production costs of EC's compared to other formulations.<sup>2</sup>

The costs associated with reformulating a pesticide product are highly variable. The chemical and physical properties of the individual AI dictate the type of pesticide (i.e., whether the product is an insecticide or herbicide) and the feasible formulations. Therefore, the use patterns and the nature of the formulation content depend to some extent on the AI. The registration costs of the product vary by the use of the product, which again is linked to the individual AI. Since it is not

TABLE 7-4. SUMMARY OF APPLICATOR EQUIPMENT COSTS<sup>a</sup>

General applicator type		Cost to purchase range, \$
Liquid applicators	Backpack sprayer	140 - 3,550
	Controlled droplet applicators	274 - 7,200
	Low-pressure sprayers	1,000 - 50,000
	Ultra-low-volume applicators	1,195 - 7,595
	Electrostatic sprayers	1,395 - 30,000
Dust applicators	Compressed air duster	200 and up
	Mechanical duster	200 and up
	Power duster	200 and up
Granule applicators	Hand-operated applicators	35 - 320
	Mechanically driven applicators	10,000 - 120,000

<sup>a</sup>John Deere Co., Moline, IL; Curtis Dyna-Products Corp., Westfield, IN; B & G Equipment Co., Plumsteadville, PA; Spyker Spreader Works, North Manchester, IN; FMC Corp., Agricultural Machinery Div., Jonesboro, AR; Earthway Products, Inc., Bristol, IN; Farm Fans, Inc., Indianapolis, IN; Top Air Manufacturing, Inc., Parkersburg, IA; London Fog, Inc., Long Lake, MN; Orchard Machinery Corp., Yuba City, CA; Gandy Co., Owatonna, MN; Reddick Equipment Co., Williamston, NC; Dempster Industries, Beatrice, NE; AgChem Equipment Co., Jackson, MN; and Ess, Inc., Athens, GA.

possible to generalize the properties of the AI's, it is difficult to generalize the costs of reformulating an AI. The cost impacts on manufacturers and consumers also cannot be generalized due to the wide variety of manufacturing capabilities and the unknown applicator equipment requirements.

### 7.3 FUMIGANTS

Fumigant use is an area not adequately addressed by the Resources for the Future (RFF) data base. The two fumigants, ethylene dibromide and dibromochloropropane, listed in the RFF data base had their agricultural uses cancelled in 1990 and 1985, respectively. This section discusses currently used fumigants, their alternatives, and the economic impacts of several scenarios in which fumigants are banned.

#### 7.3.1 Fumigants and Fumigant Alternatives

Soil fumigants currently registered for use in agricultural soils are methyl bromide, 1,3-dichloropropene (1,3-D or Telone®), chloropicrin, and metam. These AI's are available alone or in mixtures. Fumigants are general purpose compounds that control nematodes, soil fungi, soil insects, and weeds. Telone® has been under special review by the Office of Pesticide Programs (OPP) since 1986. This process reviews the risk benefit analysis of Telone® use. A decision on changes to Telone®'s registration is expected by the end of 1992. There are nonfumigant compounds that have been used on soils such as several registered organophosphates (e.g., ethoprop, fensulfothion, fenamiphos) and carbamates (e.g., carbofuran, aldicarb, oxamyl). However, these types of compounds are less effective than fumigants and are difficult to apply to the required soil depths.

#### 7.3.2 U.S. Department of Agriculture Study

An assessment of economic effects of banning soil fumigants was completed by the U.S. Department of Agriculture (USDA) in 1988.<sup>1</sup> This assessment is based on an earlier biological study of the effects of banning fumigants. It estimates how all soil-borne pests would act during a growing season to affect crop yields. The economic assessment considers the short-term effects on both crop producers and consumers if the use of all soil



fumigants were lost because of EPA cancellation, suspension, or manufacturer withdrawal. The USDA analysis did not require usage estimates in pounds of fumigant but estimates of acres planted and acres treated of the affected crops. Several scenarios were evaluated:

1. Telone® alone and in combinations is lost. All other fumigants are available plus alternatives;
2. Methyl bromide alone and in combinations is lost. All other fumigants and alternatives are available;
3. Chloropicrin alone and in combinations is lost. All other fumigants and alternatives are available;
4. Metam is lost. All other fumigants plus alternatives are available;
5. All fumigants are lost, but nonfumigant alternatives are available;
6. All fumigants and aldicarb, carbofuran, and oxamyl are lost for nematode control. Organophosphates are available; and
7. Metam, chloropicrin, and organophosphates are available. All other fumigants and aldicarb, carbofuran, and oxamyl are lost for nematode control.

The USDA concluded that producers who formerly used fumigants would be worse off by \$100 to \$200 million per year, despite higher prices, if soil fumigants were banned for citrus fruit, potatoes, tomatoes, tobacco, and a few other crops, because crop output would decline sharply. Producers who did not use fumigants would be better off by \$480 to \$800 million per year because of higher product prices received. Consumers would pay \$3.0 to \$5.1 billion more annually in the short run. Average annual consumer prices would rise 53 percent for fresh tomatoes, 11 percent for potatoes, 8 percent for canned tomatoes, and 4 percent for cigarettes. Loss of fumigants would have no effect on prices of cotton products, citrus fruit, or frozen juice.

Fumigant formulations are unique in that they do not generally contain ingredients other than the active ingredient. The VOC emissions from fumigant application are due to escape of the fumigant from the soil. Therefore, the cost impacts

described in the USDA study as a result of banning fumigants on certain crops also apply as a conservative assessment of cost impacts from controlling VOC's from fumigants by restricting fumigant use.

#### 7.4 ALTERNATIVE APPLICATION METHODS

In general, control costs for alternative application methods including ultra-low-volume (ULV) application and other methods that often increased application efficiency are unknown. Equipment costs as presented in Table 7-4 for ULV applicators and electrostatic sprayers are a factor in the overall control costs. However, no data are available to identify and contrast current use of this equipment nationwide to its potential use nationwide as a VOC emissions control alternative.

Costs associated with the pesticide formulations required for ULV and increased efficiency applications, if any, are unknown. Common pesticide formulations are likely available that may be used with high-efficiency equipment at a lower application rate, thereby minimizing added costs due to specially formulated pesticides. However, the comparison between costs of formulations currently used by a grower and costs of any new, more expensive pesticide formulations required by this control alternative is unknown. Therefore, the range of control costs for this alternative has not been estimated.

#### 7.5 MICROENCAPSULATION

No specific information is available to describe the cost impacts of reformulating solvent-containing pesticides to microcapsules. However, in general microencapsulation is an expensive or impossible production method for AI's that do not form stable emulsion systems. Microcapsules with high AI concentrations (e.g., 4 pounds per gallon [lb/gal] are more economical to produce than more dilute concentrations. The patents for high concentration production methods are held by Monsanto, therefore, these methods are not generally available to other manufacturers.

Microencapsulated formulations are mixed with water and applied in spray form. Specialized equipment is not required for

application. No costs are incurred for purchase of equipment if the grower or applicator owns spray equipment.

#### 7.6 INTEGRATED PEST MANAGEMENT (IPM)

The overall economic impact of the IPM system will be highly dependent upon the specific program used, the type of crops, and the geographical location. Advocates of the IPM concept state that "....evaluation of IPM programs in 15 States documented that IPM users overwhelmingly showed a profit while reducing their use of pesticides."<sup>11</sup> This reference further states that the farmers using IPM increased their net profits over non-IPM users by an estimated \$578 million/yr and that private pest-management consulting firms may attain revenues exceeding \$400 million/yr. These figures appear to indicate two conclusions. One conclusion is that in some States, using IPM can be cost effective compared to the more conventional farming practices. However, this depends upon a number of factors, including the type of crop, the geographical location, existing environmental conditions, the size of the farm, and the degree to which the user adheres to IPM practices. The second conclusion is that converting to IPM is neither simple nor inexpensive. Private pest-management consultants may be necessary to evaluate the individual situations, and the advice of the consultants is not free. Use of State agricultural extension service personnel, for both technical advice and consultant references, usually can be obtained at no cost and their knowledge and advice may be sufficient for many situations. Conversion to IPM practices does not occur in 1 year, and a period of time is necessary for the conversion. Overall, the IPM program can be profitable and decrease the level of pesticide consumption. The specific cost impacts depend upon individual circumstances and the farmer.

#### 7.7 REDUCED USAGE OF SELECTED PESTICIDES

No information is available to estimate the cost impacts of this VOC reduction technique.

## 7.8 REDUCED USAGE OF CROP OILS

No information is available to estimate the cost impacts of this VOC reduction technique.

## 7.9 REFERENCES FOR SECTION 7.0

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## 8.0 REVIEW OF EXISTING REGULATIONS

### 8.1 FEDERAL REGULATIONS

The distribution, sale, and use of pesticides in the United States is regulated primarily by EPA under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), enacted in 1947, and the Federal Food, Drug, and Cosmetic Act (FDCA). The FIFRA requires that all pesticides be registered with EPA, and it authorizes EPA to establish conditions for their use. The FDCA requires EPA to establish maximum acceptable levels of pesticide residues in foods. Within EPA, the Office of Pesticide Programs (OPP) administers the regulations governing pesticides.

Other branches of EPA and other Federal agencies have also adopted regulations which, though they may not be specifically targeted at pesticides, may have an impact on their use, either directly or indirectly. Under FIFRA, every State has responded by adopting its own regulations. The main restrictions that FIFRA places on States is that their regulations cannot be any less strict than those required by FIFRA, except under special limited conditions. The power to regulate pesticides does not extend beyond the State level. Attempts by local communities to adopt their own regulations have been rejected in several State courts.<sup>1</sup>

#### 8.1.1 FIFRA and FDCA

The Federal regulations under FIFRA and FDCA are summarized as they relate to particular areas including registration, labeling, restrictions on inert ingredients, application, and food residues.

8.1.1.1 Registration. Section 3 of FIFRA requires that any pesticide sold or distributed in any State be registered with OPP

prior to its sale or distribution. Section 2(u) defines a pesticide as "any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest, and any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant."

For all products not previously registered, including new active ingredients, new formulations, and new uses of registered active ingredients, FIFRA requires that the intended registrant apply for registration. In accordance with Section 3(c), an application for registration must include a complete copy of the labeling of the pesticide, a statement of all claims to be made for it, a copy of all test data supporting the claims, usage directions, the complete formula, and a request for classification for general use, restricted use, or both. The product will be registered if it meets the requirements outlined in Section 3(c)(5): its chemical composition appears to support the claims made for it, the labeling and data submitted meet the established requirements, it will perform its intended function without unreasonable adverse environmental effects, and when used as directed it generally will not cause unreasonable adverse environmental effects.

When registering a pesticide, OPP will classify it for general use, restricted use, or both as per guidelines stated in Section 3(d) of FIFRA. If OPP determines that use of the pesticide in accordance with all specified directions and normal application practices will not cause unreasonable adverse effects on the environment, then the pesticide, or the particular use for it, is classified for general use. If EPA determines that normal use of the pesticide in accordance with all specified directions may cause unreasonable adverse effects on the environment or injury to the applicator unless additional restrictions are imposed, then the pesticide, or the particular use for it, is classified for restricted use. If a pesticide is classified for restricted use, it may be applied only by or under the direction of a certified applicator. Some pesticides with several uses may be classified for restricted use and general use.

Because new pesticide registration is often a process that takes years to complete, FIFRA was amended in 1988 [Section 5(k)(3)] to require OPP to try to expedite applications for initial or amended registration of products that are similar to pesticides already registered. Similar products include those identical in composition to pesticides already registered and those that differ only in ways that do not significantly increase risks to the public health. The OPP must also expedite requests for selected minor amendments (for example, some reformulations) to existing product registrations. The 1988 amendments to FIFRA require OPP to notify the applicant in writing within 90 days of receiving the completed application whether the request is granted or denied, and if it is denied, the reasons why.

In addition to the initial registration of a pesticide, Section 4 of FIFRA requires that each registered pesticide containing an active ingredient that was first registered before November 1, 1984, be reregistered, unless the pesticide has no outstanding data requirements and it meets the initial requirements for registration under Section 3(c)(5). Due to slow progress in reregistering pesticides, the 1988 amendments to FIFRA establish tight deadlines and a fee schedule in order to expedite the reregistration process. Pesticide registrants are required to meet a sequence of deadlines for supplying the complete test data bases OPP needs to make reregistration decisions. Then OPP must meet specific deadlines in analyzing the data and making decisions. To meet the expected increase in costs associated with meeting the new deadlines, two different types of fees are levied on the industry: a reregistration fee for each active ingredient and an annual fee for registration maintenance to be assessed against individual products. These fee provisions will be in effect for 9 years, which is the time period allowed for OPP to complete reregistration.

8.1.1.2 Labeling. The FIFRA requires the following information on all labels: the name, brand, or trademark of the product; the name and address of the producer, registrant, or person for whom the product was produced; the net contents; the



product registration number; the producing establishment number; the ingredients statement; warning or precautionary statements; directions for use; and the use classification. All information on the label must be clearly legible to a person with normal vision. A draft copy of the label must be submitted with the application for registration for approval.

The ingredients statement must include the name and weight percentage of each active ingredient, the total weight percentage of all inert ingredients, and a statement of the percentage of total and water-soluble arsenic. Required warning or precautionary statements vary according to the toxicity category of the active ingredient. Highly toxic materials, Category I, must be marked "Danger." If the active ingredient is in Category I because of its oral, inhalation, or dermal toxicity, the label must be marked "Poison" in red with an adjacent skull and crossbones symbol. Toxicity Category II products must be marked "Warning," and Categories III and IV products must be marked "Caution." All product labels must be marked with the warning, "Keep Out of Reach of Children." Other warnings that may be required include "Hazard to Humans and Domestic Animals," "Environmental Hazard," and "Physical or Chemical Hazard." Directions for use must be stated in such a manner that they can be easily read and understood by persons who are likely to use them or supervise their use. A statement indicating that it is a violation of Federal law to use the product in a manner inconsistent with its labeling must be included with the directions for use along with information about application site(s), target pest(s), dosage rate for each site and pest, method of application, frequency and timing of application, reentry limitations, and storage and disposal directions for the pesticide and its container. The use classification, general or restricted, must also be on the label. If a product is classified for both depending on its particular use, then it must be marketed as two separate products with separate labels.

8.1.1.3 Inert Ingredients. In 1987, OPP released a policy statement on inert ingredients in pesticide products. This

policy statement was revised in 1989.<sup>2</sup> Under FIFRA, the majority of the data requirements and regulatory activities have focused on the active ingredient. Acute toxicity tests are required for the pesticide formulation, which includes the active and inert ingredients, but inerts had not been addressed in detail until the 1987 release of the policy statement. The policy divides the 1,200 intentionally added inert ingredients into four toxicity categories:

1. Inerts of toxicological concern (List 1);
2. Potentially toxic inerts/high priority for testing (List 2);
3. Inerts of unknown toxicity (List 3); and
4. Inerts of minimal concern (List 4).

Appendix D presents the 1989 policy statement and the compounds included on List 1. Approximately 40 inert ingredients have been identified and placed on List 1 based on their carcinogenicity, adverse reproductive effects, neurotoxicity or other chronic effects, or developmental toxicity (birth defects). For an inert to be placed on List 1, these effects must have been established by peer-reviewed data. The OPP is encouraging registrants of products containing List 1 inerts to substitute nontoxic inerts for those of toxicological concern. If the inert is not substituted, the registrant must amend the registration by changing the label to include a warning stating that the inert is present in the formulation. Pesticides containing List 1 inerts will be subject to data call-in, for which the registrant may be required to present data equivalent to that required for an active ingredient. For some inerts on List 1, OPP intends to hold hearings to collect and present information on their risks and benefits. Based on this information, OPP will determine whether products containing the inert should be cancelled, subjected to additional restrictions, or allowed to continue without change. Some of the List 1 inerts are added to formulations to act against a pest, although not necessarily the same pest targeted by the formulation. The OPP may reclassify some of these inerts as active ingredients. In addition, no new

product containing a List 1 inert ingredient will be registered unless the product is very similar to another product that is already registered.

Appendix D also presents the compounds included on List 2. Another 60 inert ingredients have been identified as potentially toxic and placed on List 2 based on their structural similarity to known toxic chemicals or data suggesting a basis for concern about their toxicity. Due to ongoing testing, List 2 is expected to change periodically. If additional testing demonstrates that the health and environmental effects of the ingredient are such that it should be placed on List 1, then the ingredient will be reclassified. The OPP has no immediate plans to issue new requirements for existing registrations containing List 2 inert ingredients. For new registrations, very similar products will continue to be registered. Applications for registration of other products containing these ingredients will be reviewed on a case-by-case basis.

List 3 and 4 inert ingredients will not be subject to any new restrictions. Inert ingredients on List 4, which includes items such as cookie crumbs and corn cobs, are considered innocuous. Inert ingredients are placed on List 3 if there is no basis for including them on any of the other lists.

For new inert ingredients, inerts not currently identified as being present in an approved formulation, or inerts that have never been present in a previously registered product, a minimal data set and scientific review will be required before the product is registered. The minimal data set will normally be a subset of the types of data required for active ingredients, including residue chemistry, product chemistry, and ecotoxicology.

8.1.1.4 Application. The EPA regulates the application of pesticides primarily through labels and labeling. Section 12 of FIFRA prohibits using a pesticide "in a manner inconsistent with its labeling." The FIFRA requires proper application methods and safety precautions to be included on the product label. Thus, anyone applying a pesticide in direct conflict with the

directions and recommendations on the label is in violation of FIFRA regulations.

When a pesticide is registered, EPA classifies it for general or restricted use. A pesticide classified for restricted use may only be applied by or under the direct supervision of a certified applicator, ensuring that these products are applied by qualified personnel. The FIFRA establishes two categories of certified applicators: private and commercial. A private applicator uses or supervises the use of restricted-use pesticides on property owned or rented by the applicator or the applicator's employer. Anyone who applies restricted-use pesticides and is not covered by the definition of a private applicator is a commercial applicator.

In most cases the State has assumed responsibility for applicator certification. In order to qualify for the right to certify applicators, a State must submit a certification plan for EPA approval. In cases where the State does not have an EPA-approved plan, EPA retains the authority to administer an applicator certification program.

The EPA has also set occupational safety and health standards for farm workers who might be exposed during and after pesticide application. Under these regulations, 40 CFR, Section 170.3, pesticide applications are restricted to conditions in which there is no risk of exposing workers or other persons who are not involved in the application, whether the exposure is caused by direct application or drift. The area to be treated should be vacated by unprotected persons before application. In addition, workers not wearing protective clothing are not allowed to enter a treated field until sprays have dried or dusts have settled. Minimal reentry times, usually 24 to 48 hours, are required for some active ingredients.

8.1.1.5 Residues. In order for a pesticide to be approved for use on food or on feed for animals used in food production, OPP must establish a tolerance, or an exemption from the need for a tolerance, for each active and inert ingredient in the pesticide. A tolerance is the maximum residue level of a

pesticide that can be legally present in raw agricultural commodities (RAC's), food, or feed transported in interstate commerce. In establishing tolerances, OPP must consider the contribution of the pesticide to the production of an adequate and economical food supply, ways in which the consumer might be affected by the pesticide, the usefulness of the pesticide, and protection of the public health. Under FDCA, the Food and Drug Administration (FDA) must monitor residues and enforce the tolerances set by OPP. The U.S. Department of Agriculture (USDA) monitors meat and poultry for pesticide residues and reports the information to EPA.

An application for registration of a pesticide will not be approved unless tolerances are established. The procedure for establishing a tolerance is covered in Section 408 of the FDCA. The applicant for registration must file a petition for tolerance, which must include product chemistry data, directions for use, toxicity data, residue data, and a statement of proposed tolerance levels for the pesticide and all of its components that are subject to regulation. The data are evaluated by the Hazard Evaluation Division (HED) of OPP, and the tolerance is granted or denied based on HED's evaluation.

#### 8.1.2 Other Federal Regulations

Other regulations that have an impact on the formulation, sale, or use of pesticides are summarized in this section.

8.1.2.1 Clean Air Act. Under the Clean Air Act (CAA), States must submit State implementation plans (SIP's) for implementing, maintaining, and enforcing National Ambient Air Quality Standards (NAAQS) for criteria pollutants in each air quality control region within the State. Emissions of volatile organic compounds (VOC's) from the application and use of pesticides may lead to an increase of ozone, a criteria pollutant for which NAAQS have been issued. To achieve attainment in this area, States may restrict the registration, sale, or use of pesticides with high VOC content.

8.1.2.2 Clean Water Act. The Clean Water Act (CWA) has historically been aimed at establishing regulations for

discharges from point sources, such as wastewater discharges from manufacturing facilities. However, Section 319 of the Act addresses nonpoint sources. This section requires that States develop and submit to EPA for approval State assessment reports and State management programs for controlling nonpoint sources of water pollution. This provides the potential for States to impose best management practices or other controls to reduce agricultural runoff from farming operations.<sup>1</sup> Options that States have include cancelling a pesticide's registration or restricting areas in which it may be used. In Wisconsin, for example, the use of aldicarb was limited to specific geographic areas after results from groundwater monitoring indicated that State-established standards had been violated. After Wisconsin imposed limitations on its use, the manufacturer of aldicarb withdrew the product from sale in the State.<sup>1</sup>

#### 8.1.2.3 1985 Food Security Act.

8.1.2.3.1 Conservation reserve program. In 1985 the USDA adopted the Conservation Reserve Program, which is designed to prevent the cultivation of fragile, erodible land. Under the program, farmers sign a contract with the USDA to retire their erodible land from crop production for 10 years and plant it with trees or other protective vegetation. In return, farmers will receive payments of up to \$50,000 per year depending on the acreage they enroll and up to 50 percent of the costs of planting trees or other vegetative cover that will prevent soil erosion. To be eligible for the program, the land must have been used for crop production for 2 of the 5 years between 1981 and 1985. The land must be too steep or too shallow, or be eroding at greater than twice the rate at which new soil is being formed.<sup>3</sup>

8.1.2.3.2 Other conservation requirements. The Food Security Act also requires that highly erodible land not placed in the conservation reserve program be protected by conservation practices by 1995 in order to reduce erosion to a specified level. Farmers not complying with the practices will be ineligible for farm benefits. Under provisions of the Act, farmers must have an approved conservation plan by 1990 and a

fully implemented plan by 1995. There are several options for meeting the requirements, including changing rotation systems, changing tillage systems, or installing permanent structures. In most cases changing to a no-till or limited-till policy is the cheapest of these alternatives. Farmers generally choose this option to meet the requirements of the bill.<sup>4</sup>

8.1.2.4 Endangered Species Act. The Endangered Species Act (ESA) requires Federal agencies to identify the risks that the products they regulate pose to endangered species and consult with the Department of the Interior for a risk analysis. If the Interior Department finds that there is jeopardy to an endangered species, it puts out a "jeopardy opinion," which is a legally binding document. In 1988 ESA was amended to include a requirement that EPA work with the Interior Department and the Department of Agriculture to identify reasonable alternatives for implementing a pesticide labeling program. The stated goal for this program is to protect endangered species from pesticides while allowing agricultural production to continue. The FIFRA requires EPA to take steps to prevent harm to endangered and threatened species from the use of pesticides. The EPA has agreed to develop a program that will satisfy the requirements of the ESA, but the programs it has proposed have been criticized and rejected for their inadequacies. The most recent program was proposed on July 3, 1989. The proposed program utilizes a threshold application rate approach for protecting endangered species without placing unrealistic burdens on pesticide users. The EPA's rationale for using this approach is based on the principle that protecting species is best accomplished by focusing on the listed species. Under the program, EPA determines and includes on the label the threshold (lowest) application rate that may affect listed species. Rates are established for the most vulnerable species first. The ranking of a vulnerable species is determined by its status and vulnerability to pesticides.<sup>2</sup> The EPA hopes to finalize the program in the spring of 1992.<sup>5</sup>

8.1.2.5 CERCLA. The Comprehensive Environmental Response Compensation and Liability Act (CERCLA) requires immediate notification to EPA's National Response Center whenever a hazardous substance is released into the environment at or in excess of the reportable quantity (RQ). Approximately 700 hazardous substances have been identified and placed on CERCLA's list, including some pesticide active ingredients, inert ingredients, and formulations. Section 103 of CERCLA exempts the application of pesticides registered under FIFRA from this reporting requirement for normal pesticide applications. The EPA has released a statement emphasizing that the exemption from reporting is limited to normal applications that are generally in accordance with label directions.<sup>1</sup>

## 8.2 STATE OF CALIFORNIA

California's regulations are the most extensive and tend to be the model for other States. A summary of these regulations is presented below beginning with the regulations which relate to registration, labeling, inert ingredients, application, and food residues.

### 8.2.1 Registration

Article 4, Chapter 2, Division 7 of the California Food and Agricultural Code requires that "every manufacturer of, importer of, or dealer in any economic poison, except a person that sells any raw material to a manufacturer of any economic poison or a dealer or agent that sells any economic poison which has been registered by the manufacturer or wholesaler shall obtain a certificate of registration from the department before the economic poison is offered for sale." An economic poison is "any spray adjuvant or any substance or mixture of substances which is intended to be used for defoliating plants, regulating plant growth or for preventing, destroying, repelling or mitigating any and all insects, fungi, bacteria, weeds, rodents, or predatory animals, or any other form of plant or animal life which is, or which the director may declare to be, a pest which may infect or be detrimental to vegetation, man, animals, or households, or be present in any environment whatsoever."



California's registration criteria are generally more stringent than EPA's. In addition to submitting to California Department of Food Pesticide Regulation (DPR) all data required by EPA, potential registrants must also include dermal absorption data and more extensive health effects studies. In accordance with Section 12825 of Article 4, the Department of Food and Agriculture may refuse to register a pesticide after a hearing:

1. If the product has demonstrated serious adverse effects within or outside the agricultural environment;
2. If the benefits of using the product are of less public value or greater detriment to the environment;
3. If there is a reasonable and practical alternative which has fewer adverse environmental effects;
4. If the use of the product is detrimental to vegetation other than weeds or to domestic animals or the public's health and safety;
5. If the product is of little use in achieving its proposed claims; and
6. If false or misleading statements have been made or implied about the product.

Section 6158 of the California Administrative Code requires that special consideration be given to several factors when a product is being reviewed, including acute and chronic health effects, toxicity to aquatic biota or wildlife, the availability of feasible alternatives, efficacy, and the potential for environmental damage, including interference with the attainment of environmental standards. All approved registrations must be renewed annually, and renewals are evaluated in accordance with procedures established for the initial registration process. This annual review provides a continuing update and evaluation of each registered product. Although pesticides registered by EPA may be denied registration in California using State guidelines, the applicant for registration of the product must be told the basis for the decision and the reasons why the decision is contrary to, different from, or inconsistent with that of EPA.

### 8.2.2 Labeling

California's label requirements are similar to those required by FIFRA. Section 6243 of the California Administrative Code states that labeling requirements shall meet but not exceed current EPA requirements. Directions for use and dilution, if any is required, must be printed on the label or enclosed in each container or package. As of September 1, 1989, the South Coast and Sacramento districts also require that the VOC content be included on the label. The California Air Resources Board, (CARB) is encouraging other districts to do the same, even though this is in direct conflict with Section 24(b) of FIFRA which restricts States from imposing or continuing in effect labeling requirements in addition to or different from those required by FIFRA.<sup>6</sup> The DPR is currently negotiating with EPA to reach an agreement which will allow districts to require this information without being in conflict with FIFRA.<sup>7</sup>

### 8.2.3 Inert Ingredients

Section 6190 of the California Administrative Code requires chronic toxicity data be reported for specific inert ingredients which are designated by the Director of the Department of Food and Agriculture. If animal feeding data are not available for these inerts, then the applicant must submit data from short-term mutagenicity tests. If these data indicate the ingredient is mutagenic, then animal feeding studies must be conducted on two species.

### 8.2.4 Application

8.2.4.1 Applicator Certification. Article 2, Section 6400 of the California Administrative code requires that restricted-use pesticides be applied only by or under the supervision of a certified private or commercial applicator. Restricted pesticides include those identified as such by EPA and any additional products which may be designated for restricted use by the DPR. In addition, under Section 14151, the Director of the DPR may specify additional pesticide applications that must be made by or under the supervision of a certified applicator. The person supervising a pesticide application must be aware of

conditions at the site of application and be available to direct and control the action of the noncertified applicator during the application process. The level of availability required shall be a function of the actual or potential hazard of the situation.

Applicants for a qualified applicator's license are examined on the laws and regulations governing pesticide use. Applicants may elect to be examined for licensing in one or more of 11 categories including agricultural pest control, forest pest control, right-of-way pest control, and landscape maintenance pest control. All licenses must be renewed annually. Applicants for a license must furnish any information that may be requested by either the county commissioner or the Director of the Department of Pesticide Regulation, including information on equipment, facilities, and operational plans for using restricted pesticides. Applicants are given an oral evaluation of their knowledge of label directions and restrictions, pests to be controlled, required protective clothing and equipment, poisoning symptoms, and awareness of surrounding environmentally sensitive areas. The license may be revoked or suspended for failure to adequately supervise the use of a restricted material, failure to comply with an applicable provision of the Code, or making false or fraudulent records or reports.

California has additional regulations, Article 1 of the Code, which govern aerial pesticide applicators. A pilot operating an aircraft engaged in pest control must have a valid pest control aircraft pilot's certificate, an appropriate and valid commercial pilot's certificate, and a current medical certificate issued by the Federal Aviation Administration. A pilot will be certified as either an apprentice or a journeyman. To receive either certificate an applicant must pass an examination demonstrating his ability to legally and safely perform aerial pesticide applications and his knowledge of the potential effects of the materials to be applied. Apprentice applicators can apply pesticides only under the direct and personal supervision of a journeyman applicator. Pest control

aircraft pilots must register with the agricultural commissioner in each county in which they work.

8.2.4.2 Conditions for Application. Section 12972 of the Food and Agricultural Code requires that all pesticides be used in a manner which prevents substantial drift to nontarget areas. Under Section 6614 of the Administrative Code, an applicator must evaluate the equipment to be used, meteorological conditions, the property to be treated and surrounding properties to determine the potential for harm or damage before applying a pesticide. The applicator should continue evaluating conditions during the application process. If the applicator determines upon evaluating these criteria that there is potential for contaminating persons not involved in the application, that there is a possibility of damage to nontarget crops, animals or property, or that there is a risk of contaminating nontarget property which may prevent normal use of that property, then no pesticide application shall be made, and if started, it should be discontinued. In addition, Section 6460 provides specific guidelines for the application of selected liquid herbicides, including 2,4-D, dicamba, and propanil. These guidelines include limits on wind speed, distance above the target from which the pesticide can be applied, and nozzle types and sizes.

Sections 6616 and 6618 of California's Administrative Code require that the owner or operator of a property be notified of and agree to any application before it is made. The property operator must then notify all persons who are known to be on the property or who are likely to enter the property. The notification must include information on the nature of the pesticide and any precautions which should be taken in accordance with the label or other applicable laws or regulations. In addition, if the pesticide is to be applied on public property, warning signs, written in English and Spanish, must be posted if there is the potential for public exposure.

8.2.4.3 Field Worker Safety. California has also adopted regulations aimed at ensuring field worker safety during and immediately after pesticide application. These regulations are

covered in Sections 6760 through 6778 of Title 3 of the California Administrative Code. The regulations are similar to those required by FIFRA. Employees are not allowed to enter a treated field until the pesticide spray has dried or the dust has settled. Specific pesticides have minimal reentry times prohibiting an employee from entering a treated area until the required time interval since application has elapsed. The regulations also require employers to orally warn employees who might be anticipated to enter an area being treated or an area that has been treated. For highly toxic pesticides, warning signs must be posted.

### 8.3 OTHER STATES

Regulations from other States are noted below either as representative examples or as unique or particularly pertinent examples relating to an area of discussion. Although this summary attempts to address current legislation, the reader should be aware that State laws and regulations are updated frequently. For example, State fees for registrations of pesticides increase on almost an annual basis. Fees in many States for 1991-1992 are markedly higher than those for 1988-1989 shown in the summary of State regulations in Table 8-1.

#### 8.3.1 Registration

Under FIFRA, States are allowed to have their own registration programs, although Section 24 of FIFRA prohibits those States from registering products that are not Federally registered. As is the case with California, the State may have stricter requirements than FIFRA, although most States base their programs on FIFRA guidelines. A State may allow additional uses for a Federally registered pesticide formulated for distribution and use within that State in order to meet specific local needs, if registration for that use has not been previously denied, disapproved, or cancelled by EPA. The EPA does reserve the right to suspend a State's registration program, if they decide that the State is not exercising adequate controls in administering its program. Details of three representative State registration

TABLE 8-1. SUMMARY OF STATE REGULATIONS

State	Registration fee pesticide, \$	Groundwater law (Y-N)	Chemigation regs (Y-N)	Pesticide use reporting regs (Y-N)
Alabama	\$50/product	N	N	N
Alaska	N	N	N	N
Arizona	\$25/product per year	Y	N	Y
Arkansas	\$25/product	N	N	Y
California	\$200/product/year	Y	N	Y
Colorado	\$70/product	Y	Y	N
Connecticut	\$60/year (multi-year)	Y	N	Y
Delaware	\$25	N	N	Y
Florida	\$20 first 10 products \$5 additional	Y	Y	Y
Georgia	\$10	N	Y	N
Hawaii	3-year/\$45 nonrestricted use or \$90 restricted use	Y	Y	Y
Idaho	Proposed	Y	Y	Y
Illinois	\$250/company, \$100/product	Y	N	N
Indiana	\$75	Y	N	N
Iowa	\$250-3000 maximum	Y	N	Y
Kansas	\$130/product/year	N	Y	Y
Kentucky	\$20/product	N	N	Y
Louisiana	\$100	Y	N	Y
Maine	\$85	N	N	Y
Maryland	\$35/product	N	N	N
Massachusetts	\$100/EPA registered product	Y	Y	
Michigan	\$15/product	N	N	N
Minnesota	\$150/product	Y	Y	Y
Mississippi	\$50/product	Y	N	Y
Missouri	\$15/product	Y	N	N
Montana	\$90/label	Y	N	Y
Nebraska	\$40/product	Y	Y	N
Nevada	\$25/product	N	N	Y
New Hampshire	\$33/product	Y		Y
New Jersey	\$200	N	N	Y
New Mexico	\$35/product	Y	N	Y
New York	\$40/product < 10, \$20 > 10	Y	N	Y
North Carolina	\$30/product	N	Y	N
North Dakota	\$25/product	N	Y	Y
Ohio	\$50/product	N	Y	N
Oklahoma	\$50/product	Y	N	N
Oregon	\$95/product	Y	N	N
Pennsylvania	\$25/product	N	N	N
Rhode Island	\$65/product	Y	N	Y
South Carolina	\$25/product, \$500 maximum	N	Y	N
South Dakota	\$75/product	Y	Y	Y
Tennessee	\$20/product	Y	N	Y
Texas	\$100/product	N	N	Y
Utah	\$15/product	N	N	N
Vermont	\$40/year	Y	N	Y
Virginia	\$125	N	Y	N
Washington	\$110/product < 25, \$105 26 < 100, \$80 101 < 150, \$55 > 150	N	Y	Y
West Virginia	Proposed	N	N	N
Wisconsin	\$100/first product	Y	Y	N
Wyoming	\$5/product	N	N	Y

programs, Virginia, Michigan, and Florida, are presented in the following paragraphs.

Although probably no State has adopted a registration program as stringent as California, each has some type of program. Potential registrants in Virginia must apply to the Department of Agriculture and Consumer Services for a certificate of registration. Section 7 of the Virginia Pesticide Law states that the registrant is responsible for the accuracy and completeness of all data submitted with the application for registration. Any subsequent claims made for a pesticide must agree in substance with representations made for the product when it was registered. If a registered product's label or formulation is later changed, then details of the changes must be submitted to the Department of Agriculture and Consumer Services.

Section 286.558 of Act No. 171 for the State of Michigan requires that any pesticide distributed, sold, or offered for sale in the State be registered in the State. Applicants for registration must submit the following for each product: a copy of the labeling, the full product name, a complete description of tests and test results, and the pesticide's complete formula, including active and inert ingredients. Registrations must be renewed annually.

Chapter 487 of the Florida Pesticide Law requires that all pesticides distributed, sold, offered for sale, delivered for transportation, or transported in intrastate commerce be registered with the Department of Agriculture and Consumer Services. Registrations must be renewed annually. If review of the data submitted with an application for registration indicates that the pesticide may have significant potential for causing adverse effects on the environment or the public health, the department shall provide a summary of the data to the Pesticide Review Council. The council may then advise the Commissioner of Agriculture regarding the registration of the pesticide. Rule 5E-2.005 of the Florida rules restricts the registration of pesticides containing ethyl or methyl parathion to uses not involving lawns, turfs or ornamental plants.

### 8.3.2 Labeling

Because Section 24(b) specifically limits additional State labeling requirements, States generally conform to FIFRA when establishing their own labeling requirements.

### 8.3.3 Inert Ingredients

Regulations and definitions for inert ingredients are similar to those of FIFRA. Total percentages of inert ingredients must be reported on the label. The complete formula, including all individual inert ingredients, must be reported when the product is registered, but this formula is held as confidential information by the States, as it is by EPA. Some States have left openings for regulating inerts as active ingredients, however. For example, in Virginia, the Commissioner of Agriculture may require any ingredient be designated as an active ingredient if, in his opinion, it enhances the effectiveness of the product to an extent that it should be considered an active ingredient.

### 8.3.4 Application

8.3.4.1 Applicator Certification. Only two States, Nebraska and Colorado, do not have EPA approved plans for certifying applicators of Federally registered pesticides. In Nebraska, EPA administers tests and issues certificates for qualified applicants. Colorado's State program requires that all commercial applicators, whether they apply restricted use pesticides or not, be licensed. The EPA certifies applicators who apply Federally restricted pesticides.<sup>8</sup>

Because of the requirement that all certification programs be approved by EPA, State certification programs for applicators using restricted pesticides are similar from State to State, although in addition to pesticides restricted by EPA, each State may classify other pesticides for restricted use. Most States require applicators be examined and certified in particular areas of pesticide use; such as field crops, forest products, structural pest control, landscape maintenance, or even for specific crops. Examinations may be written or oral, depending on the State. In some States, applicants for commercial



applicator certification must take written exams, and applicants for private applicator certification have to take oral exams.

Florida has three classifications for applicator licenses-- commercial, private and public. Public applicators use or supervise the use of restricted use pesticides while working for a public utility or governmental entity. Both public and commercial applicators are subject to the same standards.

Rule 5E-9.003 of the Rules for the Florida Department of Agriculture and Consumer Services lists the categories in which commercial and public applicators may be certified. These include agricultural plant, agricultural animal, forest, ornamental and turf, public health, industrial, institutional, structural and health-related pest control, and aerial application pest control. To be certified in one or more of these areas, applicants for certification must demonstrate their knowledge of pest control and the safe use of pesticides. Areas in which they must be knowledgeable include label and labeling comprehension, safety factors, environmental consequences, pest features, equipment characteristics, application techniques, and laws and regulations. They must also meet specific standards of competency in the area(s) in which they wish to be certified. In addition, applicants for an aerial applicator's license must submit proof of financial responsibility to be certified. Such proof may consist of depositing a surety bond with the department or obtaining an insurance policy.

Rule 5E-9-010 requires that all certified applicator licenses be renewed every four years. To be recertified an applicator must demonstrate continued competency either by retaking the basic certification examination or by accumulating the required number of continuing education units which can be obtained by attending department sponsored professional meetings or seminars.

8.3.4.2 Conditions for Application. Many States have established guidelines for pesticide applications and requirements for notification. Examples of some of these regulations are detailed in the following paragraphs.

Regulation WAC-228-185 provides guidelines for pesticide applications in the State of Washington. Under these guidelines pesticides cannot be applied in weather conditions which may promote physical drift or volatilization thereby potentially causing damage to adjacent land, humans, desirable plants or animals. Pesticides must be applied in a manner which minimizes the hazard to commercially important pollinating insect species, particularly if the application is made to or around blossoming plants, and in a manner which does not pollute water supplies, waterways, streams and lakes. The regulations also prevent the application of certain pesticides by aircraft or airblast sprayers in areas adjacent to occupied schools, hospitals, nursing homes and other similar establishments under conditions that may cause contamination of these establishments.

Section 17 of the Virginia Pesticide Law establishes standards for pesticide application equipment. The equipment must be in sound mechanical condition; it must be equipped to dispense the proper amount of material; and all mixing tanks, storage tanks, holding tanks, and components of the spray distribution system must be leakproof. Pumps for spray distribution systems must be capable of operating at a pressure which ensures an uniform and adequate rate of discharge. All application equipment must be equipped with cut-off valves and discharge orifices so that the operator may pass over nontarget areas without contaminating them. All hoses, pumps, and other equipment used to fill pesticide application equipment must be fitted with a valve or other device which prevents backflow, in order to protect water supply systems, lakes and other water sources.

North Carolina specifies conditions that must be met for aerial applications in order to reduce drift (North Carolina Administrative Code--Title 2, Section .1003). Requirements include spacing fixed nozzles on the boom to ensure a uniform spray pattern; releasing pesticides applied as liquids, in liquid carriers, or as dusts within 15 feet above the canopy of the target, except where obstructions may endanger pilot safety;

releasing pesticides applied as dry granules or pellets within 40 feet of the canopy of the target; and restricting droplet size for all restricted use pesticides and other selected liquid formulations, including paraquat and phenoxy herbicides. Section .1005 restricts areas where aerial applications can be made. Aerial applications are not allowed within 300 feet of the premises of schools, hospitals, nursing homes, churches or any occupied building used for business or social activities; on the right-of-way of a public road or within 25 feet of the road, whichever is greater; within 100 feet of any residence; and on any nontarget area where there is a good chance of causing adverse effects. For ground applications, Section 1404 states that no pesticide shall be applied under conditions that may cause drift from pesticide particulate or vapors.

Florida restricts the application of synthetic organo-auxin herbicides. Limitations on the distance which must separate the closest edge of the area to be sprayed with these compounds from nearby susceptible crops are established based on the wind speed and direction at the time of application. Droplet size is also limited. Aerial applications of these herbicides by fixed-wing aircraft is prohibited in specified areas during specific time periods.

Connecticut Public Act 88-247 requires all commercial applicators and homeowners to post signs every time they apply a pesticide or fertilizer. If neighbors file a request for notification with the Department of Environmental Protection, then they must be notified at least 24 hours in advance by telephone, by mail, or in person by the homeowner or applicator using the pesticide.

8.3.4.3 Field Worker Protection. Regulations for States concerning field worker protection are similar to FIFRA. Section .1803 of the North Carolina Administrative Code states that the reentry time shall be the period of time required for sprays to dry or dusts to settle with the following exceptions: EPA Toxicity Category I pesticides shall have a reentry time of at least 24 hours; selected pesticides, including ethyl and

methyl parathion, shall have reentry times of at least 48 hours, and in cases where the label sets more stringent requirements these shall apply. If workers must enter a field before the reentry time expires, they must be warned either orally or by posted signs of the hazards involved and the safety precautions that should be taken.

8.3.4.4 Chemigation. Chemigation is a pesticide application method in which the pesticide is mixed with irrigation water before the water is applied to the crop or soil. Because of the potential for groundwater contamination from these systems, some States have adopted regulations restricting the use of chemigation.

Regulation 16-228-232 for the State of Washington bans the application of pesticides through an irrigation system unless the registered label contains statements which specifically permit it. In situations where chemigation is allowed, the regulation requires that any person involved in any mode of operation of a chemigation system be knowledgeable about the system and under the direct supervision of a certified applicator. Specific equipment requirements are also mandated including a backflow prevention device or system in the water supply line upstream of the point of pesticide introduction; an automatic, quick-closing check valve in the irrigation line; and an interlocking control to automatically shut off the injection pump when the water pump stops or the water pressure decreases to a level which can affect pesticide distribution.

Florida and North Carolina both require antisiphon devices to prevent backflow into the water supply when irrigation systems are used to apply pesticides. North Carolina prohibits the direct connection of a chemigation system to a public water system, unless the water from the system is discharged into a reservoir tank before introducing the pesticide. In Florida applicators must use this same method or they may use a reduced-pressure-zone (RPZ) backflow preventer. Both Florida and North Carolina require extensive maintenance programs for all system

valves and switches to ensure that they are always in good operating condition.

In 1986, Nebraska enacted Legislative Bill 284 to tighten restrictions on chemigation. The bill requires applicators using a chemigation system to obtain a permit from their local natural resources district. Chemigators must pass a safety course and be certified by the State Department of Environmental Control.<sup>9</sup>

#### 8.4 REFERENCES FOR SECTION 8.0

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APPENDIX A.  
CALIFORNIA PESTICIDE DATA

## A. CALIFORNIA PESTICIDE DATA

### A.1 CALIFORNIA PESTICIDE USE REPORT

The State of California EPA, Department of Pesticide Regulation (DPR) compiles information on the annual use of pesticides in each county of the State. This information is entered into a data base and used to develop various summary reports, including the annual Pesticide Use Report (PUR). In each county, farmers and commercial applicators are required to provide selected information on the usage of each pesticide to the county, who in turn transmits the data to the DPR. Information is required for 14 different data fields and requested for 9 additional fields. At the DPR, the information is entered into computer files. Depending upon the selection of fields that are accessed, a wide variety of data can be obtained. When total pesticide usage is estimated, the use data in the PUR for restricted-use pesticides should be multiplied by 1.13 and for nonrestricted-use pesticides by 1.47 to adjust for unreported use. As discussed below, the correction factors were developed from information obtained from county agricultural staff and pesticide use permits. Table A-1 presents a summary of the information entered into the pesticide use data base. Table A-2 provides a more complete description of the fields shown in Table A-1.

For years prior to 1990, commercial applicators were required to report information on all pesticides applied in the county. A grower was required to report data only for a list of 80 restricted pesticide active ingredients and other compounds. The list of restricted pesticides is presented in Table A-3. A grower applying a nonrestricted pesticide may or may not report

this information. To correct for underreporting, a correction factor of 1.47 developed from information obtained from county agricultural staff was applied to all reported nonrestricted products in order to include the grower nonrestricted applications in the inventory. For example, if the PUR indicates that 11,323 pounds of malathion, a nonrestricted pesticide, were applied in a particular month, then the corrected usage would be:  $11,323 \times 1.47 = 16,645$  pounds.

Based on pesticide use permit information supplied by DPR, it was determined that a correction factor of 1.13 should be applied to all reported restricted use pesticide applications.

At the present time, data are collected for all pesticides used for agricultural purposes within the State; however, these data are not currently available from DPR. The most recent year for which data are available is 1987 so that data base contains entries primarily for only the restricted pesticide active ingredients.

The data compiled by DPR through the annual use survey was used to provide a basis for the volatile organic chemical emission estimates for agricultural chemicals in California. In 1983, California estimated emissions due to active ingredients to be approximately 21,800 tons. Using the data compiled for 1987, the California Air Resources Board (CARB) estimated VOC emissions due to synthetic pesticides were 32,100 tons/yr.

Depending upon the specific selection of fields accessed, a wide variety of information can be obtained. Midwest Research Institute (MRI) acquired a copy of the 1987 DPR data base, which contained more than 1,000,000 entries, and used the information to develop a variety of data aggregations. The DPR data base contained information on the quantities of active ingredients applied during 1987 but did not contain any information on other constituents of specific types of formulations. Because emulsifiable concentrates (EC's) contain quantities of organic solvents, the data presented in Tables A-4 and A-5 were developed using the data base to identify the active ingredients. The data base was searched to separate those active ingredients formulated



only as EC's and those formulated as EC's as well as other types of formulations. Using the active ingredient information, MRI searched the EPA Office of Pesticide Programs (OPP) formulation files to develop "average" or "typical" solvent content for each active ingredient in an EC. The data in Tables A-4 and A-5 show that the solvents used in these EC formulations contribute approximately 3,100 tons/yr to the VOC emissions in California.

Additional examples of different types of information displays that were derived by MRI from the data base are shown in Tables A-6 to A-12. For each active ingredient, Table A-6 shows the quantity of the active ingredient used in all of the types of formulations. This type of table is very useful in showing the major and minor formulations for each active ingredient. Table A-7 shows the quantity of each active ingredient used in each of 12 different pesticide types. In Table A-8, agricultural and non-agricultural uses are shown for each active ingredient. Many active ingredients are formulated as an EC and applied to crops by aerial spraying. For each active ingredient, Table A-9 provides data for the quantity of active ingredient and the quantity of solvent used to form the EC, the quantity of each EC applied using ground spraying, aerial spraying, and other application methods, and the average application rates (lbs per acre) for ground and aerial spraying. Table A-10 provides data on total pesticide active ingredient usage in each of the 58 counties. Thirteen counties used one million pounds or more of active ingredient and the five counties with the highest usage accounted for 46% of the total use in the State. Table A-11 shows the total quantity of active ingredients used on each commodity; the two commodities with the highest usage are strawberries and cotton. The use of each active ingredient by month can be tracked as shown in Table A-12. Application of the pesticides is highest in September and lowest in January. Similar information could be obtained by other States if an information collection system for pesticide usage was available within the State.

## A.2 CROP OILS (NONSYNTHETIC OILS)

An Air Resources Board (ARB) survey of pesticide oil determined the 1981 statewide use of pesticide oils in four categories: carrot oil, weed oil, foliar oil, and dormant oil. Survey forms were sent to manufacturers and distributors of pesticides and pesticide oils requesting information on the description of the oil, registration number, quantity sold, approximate percent sold directly to users, and use (e.g., agricultural, home and garden, institutional). No data are available for any years since 1981. The PUR reported the county use of pesticide oils in six categories: petroleum hydrocarbons, mineral oil, petroleum oil unclassified, petroleum distillate, petroleum distillate aromatic, and aromatic petroleum solvents. However, the amount of pesticide oil listed in the PUR was incomplete since not all users were required to report these data.

Based on the results of the survey, the ARB estimated emissions from the use of all pesticide oils in California to be approximately 18,600 tons in 1987. The California DPR, has estimated the use data for pesticide oils (i.e., crop oils or nonsynthetic oils) in 1990 to be 13,615 tons. This shows a decrease of almost 5,000 tons from the 1987 use level.

## A.3 CARB EMISSIONS ESTIMATE METHODS

The data generated for the 1983 PUR was used by the California Air Resources Board (CARB) to calculate an emissions inventory for pesticide applications from all sources in the State. The most recent year for which PUR data are available was 1987. The methods used by CARB to estimate emissions due to various mechanisms are presented in the following sections.<sup>1</sup>

As stated on page 4-1-A-2 of the CARB estimation methods, emissions are not calculated for chemicals with unknown vapor pressure or a vapor pressure of less than  $10^{-7}$  mm Hg. In addition, pesticides having only inorganic constituents are not considered to be sources of VOC emissions.

A.3.1 Emissions During Application. The following equation was used to calculate volatile organic emissions during application:

$$A_2 = A_1 \{1 - [(4.625) (\log P_i + 7) (0.0024T^2) (0.01)]\}, \quad (\text{Eq. 1})$$

where:

$A_2$  = pounds of pesticide AI deposited after emission loss during application per acre;

$A_1$  = pounds of pesticide AI applied;

$P_i$  = vapor pressure of pesticide i at 20°C in mm Hg;

$T$  = average temperature in the month of application in degrees centigrade; and

$A_1 - A_2$  = emissions in pounds during application through immediate evaporation.

This equation is based on data indicating that application losses of a pesticide seem to have an approximately linear relationship to the log of the vapor pressure and are approximately proportional to the square of the temperature within the range of 5° to 30°C.<sup>1</sup>

A.3.2 Pesticide Loss by Sorption. Adsorption and absorption rates for pesticides vary depending on the chemical nature of the pesticide, meteorological conditions, and the application site. Most sorption processes are reversible. For most pesticides, only a small percentage is irreversibly adsorbed and unavailable for evaporation. Because of the variables involved, it is impossible to determine a value for sorption loss for every pesticide application.

The CARB assumed that 2 percent per month--that is, 2 percent of the amount of pesticide deposited--is lost through sorption and is unavailable for evaporation. For highly volatile pesticides (vapor pressure  $\geq 0.3$  mm Hg), it was assumed that none of the deposited pesticide will be lost by sorption.

A.3.3 Pesticide Loss by Degradation. Pesticides are degraded in the environment by a number of mechanisms, including chemical, photochemical, and biological degradation. Although most pesticides are susceptible to one or more of these degradation mechanisms, the quantity of hydrocarbon compounds

available for vaporization and atmospheric reaction is not necessarily reduced. A pesticide may be split into two smaller compounds by degradation mechanisms, but this does not change the total mass available for evaporation. The ultimate degradation products of an organic compound under favorable environmental conditions are carbon dioxide and water, but studies indicate that most pesticides are not degraded to that point.

Although there is no established procedure or model for predicting degradation losses for pesticides, it is apparent that some portion of most pesticides is unavailable for evaporation due to degradation processes. Degradation losses were assumed to be 4 percent per month of the pesticide remaining after sorption losses for nonsynthetic hydrocarbon pesticides and is therefore unavailable for evaporation.

A. Nonacreage Applications.. Nonacreage applications are pesticide applications that are referenced in units other than acres, such as head of livestock, tons of produce, and number of bins. For nonacreage pesticide applications, emissions during application are calculated using Equation 1. Pesticide losses due to sorption and degradation are also calculated. The amount of pesticide remaining after subtracting these losses is assumed to evaporate in the month of application.

A.3.4 Maximum Possible Evaporation Rate of Deposited Pesticides. Although several methods have been proposed in the literature for estimating volatilization losses of pesticides from soil surfaces, many of these methods require input data that are not readily available on a wide-scale basis. The method used by CARB is based on a model developed by Hartley and modified by Spencer.<sup>2,3</sup> The method is based on the principle that the rate of loss of a pure substance into the atmosphere from an inert surface is governed by two of the substance's properties: the saturation vapor concentration and the rate of diffusion through the still air layers bounding the treated surface. The modified equation for estimating the evaporation rate is:

$$E_p = \frac{EA}{1-RH} \times \frac{P_i (M_i)^{1/2}}{P_w (M_w)^{1/2}}, \quad (\text{Eq. 2})$$

where:

$E_p$  = the maximum evaporation rate of compound  $i$  in pounds per acre (lb/acre) during the month under consideration.  $E_p$  is calculated for each month that pesticide is available for evaporation;

$EA$  = adjusted water evaporation rate in lb/acre;  $EA = 0.73E$ ,  $0.40E$ , and  $0.70E$  for application to vegetated land, soil surfaces, and water surfaces, respectively;

$E$  = inches of water evaporated in the month  $\times 226,600$  lb/in. of water on one acre;

$RH$  = average relative humidity during the month;

$P_i$  = vapor pressure of compound  $i$  at cited temperature;

$M_i$  = molecular weight of compound  $i$ ;

$P_w$  = vapor pressure of water at temperature cited for  $P_i$ ; and

$M_w$  = molecular weight of water.

In calculating emissions, applications of insecticide, fungicide, defoliant, and insecticide-herbicide mixtures are considered to be applications to a vegetated surface, while herbicide and nematicide applications are considered to be applications to a soil surface.

**A.3.5 Monthly Emissions From Deposited Pesticides.** Monthly emissions from the volatilization of deposited pesticides for acreage application are calculated using the evaporation rate,  $E_p$ , calculated using Equation 2. The monthly emissions are calculated as follows:

$$kt = 2.303 \log \frac{A_4}{A_4 - A_x}, \quad (\text{Eq. 3})$$

where:

$k$  = the rate constant ( $\text{day}^{-1}$ );

$t$  = time in days;

$A_4$  = pounds of deposit per acre available for evaporation in a given month; and

$A_x$  = pounds of pesticide i evaporated per acre in any month for a time t.

The rate constant, k, is calculated for each month that pesticide i is available for evaporation by substituting  $E_p$ /number of days in the month for  $A_x$  when  $t = 1$  day.

The amount of pesticide evaporated each month,  $A_x$ , is then calculated by using the calculated rate constant, k, and setting  $t$  = the number of days in the month. Total monthly emissions can then be calculated by multiplying  $A_x$  by the number of acres in the application and adding the emissions during application calculated using Equation 1.

If  $A_4 - A_x$  is less than 0.1 lb/acre, then it is assumed there is no pesticide remaining to evaporate in the next month. If  $A_4 - A_x$  is greater than 0.1 lb/acre, then the pesticide carryover and resulting emissions are calculated until the remaining amount is less than 0.1 lb/acre or 12 months of carryover have occurred, whichever comes first.

A.3.6 Maximum Evaporation Rate and Rate Constants for Application to Vegetated Surfaces. For a pesticide applied to foliage, a portion is deposited on plant leaf surfaces and a portion falls through and is deposited on the soil surface. For example, Grove et al. reported that the crop canopy intercepted 52 percent of 2,4-D ester applied to a wheat field.<sup>4</sup> Taylor et al. reported on field experiments in which a mixture of dieldrin and heptachlor were applied to an orchard grass field.<sup>5</sup> Analysis of soil and grass residue immediately after application showed grass residues of dieldrin were approximately four times greater than soil residues, while grass residues of heptachlor were approximately two times greater than soil residues.<sup>5</sup> From these results it is obvious that the percentages deposited on each surface vary substantially, even when two pesticides are applied simultaneously, as in the Taylor experiments.<sup>5</sup> Because both studies indicate that at least half of the amount applied is deposited on the plant surfaces, CARB assumed in calculating emissions that 50 percent is deposited on the plant surfaces and 50 percent on soil surfaces.

Evaporation from the pesticide deposited on the foliage is generally much faster initially than evaporation of the portion deposited on the soil. These losses are actually more rapid than those predicted using Equations 2 and 3. Equation 3 was modified to compensate for the greater-than-expected losses from vegetated surfaces by multiplying the rate constant,  $k$ , in Equation 3 by eight, so that predicted losses matched experimental losses more closely. This adjustment to the rate equation is only applied to the half of the pesticide deposited on the foliage and is only used for calculating emissions during the month of application.<sup>5</sup>

#### A.3.7 Rate Constants for Soil-Incorporated Pesticide.

Volatilization is greatly inhibited for pesticides incorporated into the soil after application. Several models have been developed for predicting volatilization of soil-incorporated pesticides, but these models require input data that are not available on a wide scale. Because the differences in volatilization are so large and incorporation is a common practice, CARB addressed these cases, even though the method used was not ideal. For the purposes of CARB, an approach is used that is similar to the one used for pesticides applied to foliage. Based on the data from Glotfelty and Taylor, comparing volatilization losses of soil-incorporated pesticides to losses for nonincorporated pesticides, the rate constant is divided by 500 when calculating monthly emissions from soil-incorporated pesticides.<sup>6,7</sup> Although differences in volatilization losses vary depending on the extent of incorporation, the pesticide used, and soil conditions, the factor of 500 is an average difference based on percent loss per day between pesticides that are incorporated and nonincorporated.

#### REFERENCES FOR APPENDIX A

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TABLE A-1. DPR PESTICIDE USE DATA

Data Field Name	Format	Description	Use
1. Record ID	1	record identification	identification
2. Process date month year	2 1	date of processing of data	date record no known use
3. Batch number	3	batch number	batch number record
4. County number	2	county number	county identification used to characterize spatial pattern of pesticide usage
5. Locators section township township direction range range direction base and meridian	2 2 1 2 1 1	section township township direction as North or South range range direction as East or West base and meridian as Humboldt, San Bernardino, or Mt. Diablo	identify exact location of pesticide application location data is not available for all pesticide applications
6. Date applied month day year	2 2 1	date of pesticide application	used to characterize temporal pattern of pesticide application
7. Commodity code	4	numeric code of commodity treated	identifies the commodity that the pesticide is applied to
8. Applied method	1	method of application (e.g., ground rig, air)	used in emissions inventory calculations and helpful in studies of varying emission rates since application method influences loss (e.g., air application results to greater drift loss)
9. Acres/unit treated	8	total acreage or units treated	indicates extent of pesticide application
10. Type unit	1	unit of measure of commodity treated, such as acres, head of livestock, tons of produce, etc.	to indicate unit of measure
11. Registration number firm number label number revision code sub-registration number	5 5 2 5	each pesticide product has been assigned a registration number consisting of a firm number, product number, revision code and sub-registration number	pesticide identification reference
12. Total product used Total product applied Unit of measure Decimal code	8 2 1	amount of pesticide applied unit of measure decimal code	used to define amount of application no known use
13. Document number	6	number of pesticide usage reports received by CDFW	no known use
14. Summary code	1	count of number of documents	no known use
15. Type	1	type of pesticide (e.g., herbicide, fungicide)	used to determine pesticide category

TABLE A-1. (Continued)

Data Field Name	Format	Description	Use
16. Use	1	category of pesticide use (e.g., agricultural, hospital, non-crop)	used to determine use category
17. Formulation code	2	code of the form in which the pesticide is marketed (e.g., wettable powder, emulsifiable concentrate, bait, etc.)	information regarding method of application
18. Chemical code	2	code to designate chemical class (e.g., acids, arsenics hydrocarbons, carbonates, etc.)	chemical classification and identification
19. Chemical percent	5	percentage chemical content of the pesticide	used to determine amount of actual ingredient
20. Chemical alpha code	6	code of chemical product (e.g., atrazine, 2-4-D)	chemical identification
21. Commodity alpha code	6	commodity code	commodity identification
22. Total pounds active ingredient	12	amount of active ingredient in the pesticide	considered the amount of pesticide used

TABLE A-2. TAPE FORMAT-1984 AND AFTER

Column #	Field	Description of field
1	Record type	1 - individual pesticide use reports 2 - monthly pesticide use reports 3 - corrections
THE FOLLOWING IS FOR RECORD TYPE 1, INDIVIDUAL USE REPORTS		
2 - 77		This information is keyed in from the pesticide use reports we receive from the counties.
2 - 7		For internal use only
8 - 9	County Number	Refer to attachment A for list of counties
10 - 18	Locators	Section, Township, Township dir., Range, Range dir., Base & Meridian
19 - 23	Date Applied	Date pesticide was applied to above location
24 - 27	Commodity code	Commodity treated - refer to attachment B
28	Application method	G - Ground application A - Aerial application O - Other type of application
29 - 36	Acres/Units Treated	A numerical amount of acres or units treated for this application. 8 digit field, with 2 places to the right of the decimal.
37	Type Unit	A - Acres U - Units T - Tons P - Pounds C - Cubic feet K - Thousands of cubic feet S - Square feet
38 - 58	Registration #	EPA Registration number of the product applied
59 - 67	Total Product Applied	Amount of product applied 9 digit field, with 4 places to the right of the decimal.
68 - 69	Unit of Measure	GA - gallons QT - quarts PT - pints OZ - ounces LB - pounds GR - grams ML - milliliters LI - liters KG - kilograms
70		For internal use only

## ATTACHMENT C TO TABLE A-2

### TYPE CODES

A = Adjuvant (spreader, sticker, wetting agent) or Water Modifiers  
 B = Algeacide  
 D = Disinfectant (or Bacteriostatic or Water Conditioners)  
 E = Fungicides (boats, aquariums, paint)  
 F = Herbicides (plant killer, weeds)  
 G = Insecticides (also for snails and Miticide)  
 H = Nematicide  
 J = Rodenticide (and fish and birds)  
 L = Fungicide & Insecticide  
 M = Fungicide & Herbicide  
 N = Herbicide & Insecticide  
 O = Fungicide, Herbicide & Insecticide  
 P = Growth Regulator ( and root tone and thinning)  
 R = Repellent  
 Q = Defoliant (and Desiccant)

### USE CODES

A = Agricultural  
 B = Home Garden  
 C = Hospital  
 D = Household  
 E = Industrial (if lots of things listed including Hospitals--code  
     Industrial--list Hospital and other things as commodities)  
 G = Manufacturing (and formulating growth regulators)  
 H = Residential (done by licensed people)  
 I = Structural  
 J = Swimming Pools (spas and hot tubs also)  
 K = Non-Crop (non-selective weed killer)  
 L = Turf Areas  
 M = Domestic Animals (used on them)  
 N = Nursery  
 O = Spreader Sticker  
 P = Soil Fumigation  
 Q = Agricultural Disinfectant  
 R = Agricultural Commissioner

### FORMULATION CODES

1 = Bait	9 = Liquid (and spray pumps)
2 = Coating (and paints and salves)	10 = Oil
3 = Dust	11 = Pressurized Dust
4 = Emulsifiable Concentrates (or Emulsifiable Liquid)	12 = Pressurized Fumigant
5 = Fertilizer	13 = Self-Generating Smokes
6 = Gels, Pastes (and creams)	14 = Pressurized Sprays (and foggers and aerosols)
7 = Granular, Tablets (such as briquets, solids)	15 = Wettable Powder (& dry flowable)
8 = Impregnated Material (such as ear tags collars)	16 = Soluble Powder

(codes 4, 9, 10 all are reported in liquid measurements)

TABLE A-3. LIST OF RESTRICTED PESTICIDES

I. Insecticides

1. Aldicarb (Temik)
2. Aldrin
3. Carbaryl (Sevin)
4. Carbofuran (Furadan)
5. Carbophenothion (Trithion)
6. Chlorobenzilate
7. Chlordimeform (Fundal)
8. Azodrin (Monocrotophos)
9. Bidrin (Dicrotophos)
10. Dialifos (Torak)
11. Dieldrin
12. Demeton (Systox)
13. 4, 6 Dinitro-o-cresol (Dnoc)
14. EPN
15. Chlordane
16. Di-syston
17. Endosulfan (Thiodan)
18. Ethion
19. Guthion
20. Heptachlor
21. Lindane (Gamma-BHC)
22. Methomyl (Lannate)
23. Methyl Parathion
24. Mocap (Ethoprophos)
25. Monitor
26. Endrin
27. Naled
28. Nema-cur (Fenamiphos)
29. Ompa (Schradan)
30. Parathion
31. Phorate (Thimet)
32. Phosdrin

TABLE A-3. (Continued)

33. Phosphamidon
34. Phostoxin
35. Supracide
36. Starlicide
37. Avitrol
38. Tepp (Sulfotepp)

II. Herbicides

1. 2, 4-D
2. 2, 4-D Amine Salt
3. 2, 4-D Butyl Ester
4. 4 (2-4-DB) Isoctyl Ester
5. 4 (2-4-DB) Butoxyethanol Ester
6. MCPA Dimethylamine Salt
7. MCPA Isooctyl Ester
8. Propanil
9. Paraquat Dichloride
10. Def/Folex
11. DNBP (Dinoseb)
12. 2-4-OP
13. 2, 4-5T
14. 2, 4 Dinitrophenol
15. Dicamba
16. Picloram
17. Silvex (Fenoprop)
18. Nitrofen (Tok)

III. Nematocides

1. Chloropicrin
2. DBCP
3. Methyl Bromide
4. 1, 3 Dichloropropene (Telone)
5. Ethylene Dibromide
6. Ethylene Dichloride

TABLE A-3. (Continued)

IV. Adjuvants

1. Diethylamine Salt of Coconut
2. Triethanolamine

V. Others

1. Cadmium containing pesticides
2. Calcium Cyanide
3. Carbon Bisulfide
4. Carbon Tetrachloride
5. Compound 1080
6. Dasanit
7. DDD (no longer manufactured)
8. DDT
9. Inorganic Arsenicals other than Sodium Arsenite
10. Mercury containing pesticides
11. Sodium Cyanide
12. Sodium Arsenite
13. Strycanine
14. Telone (DD)
15. Toxaphene
16. Zinc Phosphide

TABLE A-4. ACTIVE INGREDIENTS USED ONLY IN EC FORMULATIONS (1987)

Active ingredient	Quantity of active ingredient (pounds)	Solvent (pounds)	Total Act. + Sol. (pounds)
Tributylphosphorotrithioate	749,282	281,645	1,030,927
Profenofos	450,102	193,859	643,961
Methidathion	411,038	1,138,777	1,549,815
Merphos	229,738	86,356	316,094
Pebulate	127,401	26,501	153,902
Oxyfluorfen	89,903	194,326	284,229
Diclofop-methyl	60,517	92,906	153,423
Sulprofos	42,562	8,924	51,486
Bensulide	40,289	40,289	80,578
Diethatyl-ethyl	26,848	30,196	57,044
Chlorobenzilate	24,910	25,457	50,367
Metolachlor	22,264	<5%	22,264
Demeton	15,526	14,851	30,377
Bromoxynil, butyric acid ester	7,671	24,590	32,261
TOTAL	2,298,051	2,158,677	4,456,728



TABLE A-5. ACTIVE INGREDIENTS USED IN EC AND OTHER FORMULATIONS (1987)

Active Ingredient	EmulConc (lbs)	Solvent (lbs)	Liquid (lbs)	Fumigant (lbs)	Wet. Powder (lbs)	Gran. Tab. (lbs)	PresSpray (lbs)	Dust (lbs)	Other (lbs)	Total (lbs)
Methyl bromide	178,802	<2%	2,697,167	5,969,582	229,982		257,196			9,132,747
Propargite	1,499,325	300,235			314	1,186,784		82		2,119,624
Molinate	487,847	Water	181,489		282,179	8,702		30		1,674,945
Parathion	308,034	105,184			28,761	3,243				883,618
Chlorpyrifos	743,841	915,075			597,664	22,083		14,575	26,647	1,690,120
Carbaryl	37,809	42,115	35,106		493,973			37,638		775,809
Maneb	151,872	701,273	17,990		504,253			5		1,402,546
Azinphos-methyl	36,162	107,358	337,831							649,778
MCPA, dimethylamine salt	182,928	Water	129,391			241,719				500,757
Trifluralin	101,822	94,657	19,247		138,428			2,906		567,689
Endosulfan	283,848	526,649	65,186		5,631			15,325		971,079
Malathion	275,293	44,368	259,073							405,803
2,4-D, dimethylamine salt	58,987	Water	184,885							317,060
Elthephon	109,322	72,224	23,985							366,231
Diazinon	71,146	50,310	754		154,723	30,780		920		331,864
Dicofol	242,297	263,842	123,585		2,891			12,558		522,142
Chlorothalonil	75,305	96,182	15,454		27,495			7,236	26	322,547
Naled	202,968	68,252	209,430							293,936
Metam-sodium	5,150	Water			183,553					214,580
Diuron	17,414	Water	59,157							200,967
Pendimethalin	132,872	139,440	129,794							330,269
Methyl parathion	53,171	51,762	15		180			96		235,003
Gibberellins	159,677	Water	53,936		33				1,457	161,182
Sodium cacodylate	106,495	Water	804							160,431
Deutolton	106,216	8,747	3,829		69,587	25,878				141,445
Simazine	8,589	Water			4,158	42,561				124,666
Phosphane	90,145	142,114	70,034							236,417
Bromoxynil octanoate	21,182	15,146	5,153							106,372
Monocrotophos	69,656	46,859	35,039							121,668
2,4-D, alkandamine salt	34,114	Water								69,153

TABLE A-5. (continued)

Table 2. Active Ingredients Used in EC and other Formulations										
Active Ingredient	EmulConc (lbs)	Solvent (lbs)	Liquid (lbs)	Fumigant (lbs)	Wet. Powder (lbs)	Gran. Tab. (lbs)	PresSpray (lbs)	Dust (lbs)	Other (lbs)	Total (lbs)
Fenamiphos	66,830	105,019				1,340				173,189
Naopropate	12,564	40,733			45,105	5				98,407
2,4-D, butoxyethanol ester	12,789	6,274	31,838							50,701
Ethion	29,528	18,036	609		8,269	152		951	2,150	59,695
4(2,4-DB), dimethylamine salt	7,099	Water	33,864							40,933
Phosphamidon	21,832	4,392	17,832							44,156
Fenofos	33,400	31,564				3,027				67,991
EPTC	35,130	2,717	753			45				38,645
Carboxylic acid	18,143	Water	9,189							27,312
Vinclozolin	4,548	5,583								27,499
Dicamba, dimethylamine salt	5,270	Water	16,488		17,368					21,758
2,4-D	3,299	2,706	8,782			10				14,777
2,4-D, n-octyl, 1,3-propylenediamine salt	3,971	3,982	7,485							15,438

Note: The manufacturer of chlorothalonil has stated that this active ingredient is not formulated as an EC. The information presented in this table was obtained from the California PUR and EPA Office of Pesticide Programs files.

TABLE A-6. ACTIVE INGREDIENT BY FORMULATION TYPE (1987)

Active Ingredient	Liquid	EmulCoat	Pumigant	Wet Powder	Gran.Tab.	Sol. Powder	FreeSpray	Dust	Ball	Oil	Cela,Pastes	Total
1,3-dichloropropene	13,648,857											13,648,857
Methyl bromide	2,697,167	178,002	5,990,502				257,196				518	9,133,265
Chloropicrin	875,066	3,649	1,487,164				123,604					2,489,573
Propargite		1,498,325		229,902				82				1,729,389
Molinate		487,847		314	1,186,784							1,674,945
Ziram	222,874			674,730	16,611							914,215
Permethrin	181,489	304,034		282,179	8,702			30				778,434
Chlorpyrifos		743,041		28,761	3,243							775,045
Tributylphosphorotribionate		749,282										749,282
Carbaryl	35,106	37,609		597,664	22,093			14,575	26,647			733,694
Malathion	17,990	151,672		493,973				37,438				701,273
Asiphos-methyl		36,162		504,253				5				542,420
MCPA, dimethylamine salt	337,831	162,926			241,719							500,757
Trifluralin	129,391	101,922										473,032
Profenofos		459,102										450,102
Endosulfan	19,247	283,849						2,906				444,430
Chlorthal-dimethyl					585							436,544
Metidathion		411,038										411,038
Thiobencarb												404,510
Malethion	65,186	275,293		5,631	404,510			15,325				361,435
Captaon	3,655			285,083				59,894				348,632
2,4-D, dimethylamine salt	250,073	58,987										317,060
Ethionphos	184,685	108,322										294,007
Olyphosate, isopropylamine salt	283,074											283,074
Diazinon	23,985	71,146		154,723	30,780			920				281,554
Acaphos				371				24,152				280,857
Carbofuran	138,462	242,297		2,891	131,447							269,909
Dicofol	754											258,500
Meibumidophos	251,427							12,558				251,427
Aldicarb					242,750							242,750
Merphos		228,738										228,738
Chlorothalonil	123,565	75,305		27,495								226,365
Naled	15,454	202,948										225,404
Mezam-sodium	209,430	5,159						7,236	26			214,580
Duron		17,414		183,553								200,967
Prodimethalin	59,157	132,672		180								191,829
Methyl parathion	129,794	53,171										183,241
Formetanate hydrochloride												180,227
Cyomazine	143,258											167,751
Bentazon, sodium salt	165,770			3,084								165,770
Gibberellic	15											161,182
Sodium cacodylate	53,896			33								160,431
Dicbloran		159,677										145,442
Phorate		106,495										140,774
Phorate				128,569								132,698
Deffolates	604	106,216			140,774							127,401
Pebulate		127,401			25,878							124,666
Sesamine	3,929	8,589										121,485
Hydrogen cyanamide												117,729
Phosmet	121,485											

TABLE A-6. (Continued)

Active Ingredient	Liquid	Emul Conc	Fumigant	Wet Powder	Gran. Tab	Sol. Powder	Press Spray	Dust	Bait	Oil	Gels, Pastes	Total
Crystalin	113,600			707		184						114,491
Iprodione				104,719								104,719
Phosalone		90,145		4,158								94,303
Bromoxynil octanoate	70,034	21,192										91,226
Oxyfluorfen		89,903										89,903
Propoxazamido				18,218		59,804						78,022
Folpet				77,146								77,146
Monocrotophos	5,153	69,656										74,809
Hexazinone	45,191			4,440		23,833						73,464
Propenil	70,929											70,929
2,4-D, allanilamine salt	35,039											69,153
Fenamiphos		34,114			1,340							68,170
Thiophanate-methyl		66,830						124				64,032
Dicofop-methyl	2,951	60,517				5						60,517
Napropamide		12,564										57,674
Triadimenol												52,676
Acroclon			50,210									50,210
Alachlor	45,049											45,049
Dechloropropene-dechloropropene	4,236											44,933
2,4-D, butoxyethanol ester	31,638											44,427
Sulprofos												42,562
Ethion	609											41,659
Fenbutatin-oxide	18,108											41,271
4(2,4-DB), dimethylamine salt	33,864									1,843		40,933
Bernathide		7,069										40,289
Phosphamidon		40,289										39,764
Diquat dibromide	17,832											39,757
Prometryn	36,757											38,517
Maleic hydrazide	35,460											37,866
Fenofos	792											36,427
EPTC	753											35,928
Avialazine		33,400										35,216
Oxamyl	32,993											32,993
Prothion	28,945	1,346										32,554
MSMA	31,735	802										32,537
Bromacil												30,274
PCNB	27	4										30,264
Berofen	309											29,066
Cyfluthrin												28,483
Caecothic acid	9,169	18,143										27,312
2,4-D, 2-ethylhexyl ester	26,439	781										27,220
Disbuthyl-ethyl		26,848										26,848
Chlorobenzilate		24,910										24,910
Metolachlor		22,264										22,264
Vindoxin		4,548										21,916
Documba, dimethylamine salt	16,488	5,270										21,758
Atrazine	14,220											21,493
Captafol	6,494											20,488
2,4-D, diethanolamine salt	20,043											20,043

TABLE A-6. (Continued)

Active Ingredient	Liquid	Emul Conc	Fumigant	Wet Powder	Grav. Tab	Sol. Powder	Frost Spray	Dust	Bait	Oil	Gels/Pastes	Total
Chloromaron	18,152			19,904	1,185							19,904
Permethrin		15,526										19,337
Deltamethrin	15,208											15,526
2,4-D, trisilylamine salt	8,762	3,299			10							15,208
2,4-D	7,485	3,971										12,071
2,4-D, n-octyl 1,3-propylenedisiamine salt				518	4,229	5,855						11,456
Metribuzin		7,671										10,602
Bromoxynil butyric acid ester												7,671
Total	21,228,262	8,390,104	7,577,651	4,919,133	2,587,643	550,226	300,890	193,365	26,673	1,843	518	45,856,308

**PRINTED TYPE**

**A-25**

TABLE A-7. (continued)

## PESTICIDE TYPES

Active Ingredient	Neemite	Pungit/Herbicide	Herbicide	Pungit	Defoliant	Growth Reg.	Pungit/Herb	Defoliant	Dwarfing	Rootkilling	Total
Oryzin			114,491	104,710							114,491
Ispodione											104,710
Phosalone		94,391									94,391
Bromopropyl acetate			91,226								91,226
Oxyfluorfen			88,003								88,003
Propargyl			78,022	77,146							78,022
Polyp											77,146
Monocrotophos		74,000									74,000
Hexachlor			73,464								73,464
Propyl			70,929								70,929
2,4-D, dimethylamine salt			68,153								68,153
Phenylphos				64,032							64,032
Thiophanate-methyl			64,517								64,517
Dithiopy-methyl			57,675								57,675
Napropamide				52,676							52,676
Trifluralin			50,210								50,210
Azinphos			45,049								45,049
Abolter										2,466	
Dichloropropene-dichloropropene	2,223	48,344									
2,4-D, butylphthalate ester											
Sepridin			42,542								42,542
Eticon			41,658								41,658
Perbutazine-oxide			28,435								28,435
4(3,4-DIB), dimethylamine salt											
Benazide											
Phosphamidon			38,764								38,764
Diquat dibromide			38,757								38,757
Proxypyr			38,517								38,517
Melaleucaldehyde						37,045					37,045
Fluorfen			36,426								36,426
EPIC			35,928								35,928
Azinphos				34,316							34,316
Oxymyl			32,994								32,994
Propham			32,553								32,553
Metolach			32,536								32,536
Bromsal			30,271								30,271
PCNB				9,070							9,070
Benlate			28,065							28,392	28,065
Oxymyl			28,483								28,483
Oxamyl acid			5,292								5,292
2,4-D, 2-ethylhexyl ester			27,229		22,008						27,229
Dithiopy-methyl			26,940								26,940
Chlorobutyl			24,910								24,910
Metolach											
Vindocin			22,264								22,264
Disulfen, dimethylamine salt				21,915							21,915
Azinphos			21,757								21,757
Capital			21,491								21,491
2,4-D, dimethylamine salt			20,943								20,943

TABLE A-7. (continued)

Active Ingredient	Pesticide Type										
	Neem Oil	Fungicide/Insect	Insecticide	Herbicide	Fungicide	Dafidant	Greenhouse	Fungicide/Insect	Disinfect	Endosulfan	Total
Chlorpyrifos			10,337	10,004							10,004
Permethrin			15,536								15,536
2,4-D, dichlorophenoxy acid				15,200							15,200
2,4-D				12,050			13				12,071
2,4-D, o-chloro 1,3-propylenedioxy acid				11,456							11,456
Monobutyl				10,602							10,602
Benzoic acid ester				7,671							7,671
Total	11,004,000	10,534,700	0,003,075	7,204,943	3,000,770	1,130,574	400,005	357,756	35,041	3,362	45,856,366

Note: The manufacturer of chlorothalonil has stated that the active ingredient is not used as a herbicide. However, the 5,367 pounds shown in this table were reported in the 1987 California PUR as being used as a herbicide.



TABLE A-8. PESTICIDE CONSUMPTION IN 1987 BY USE AREA

Active Ingredient	Pesticide Use								Total
	Soil Fumigation	Agricultural	Non-Crop	Industrial	Turf Areas	Nursery	Home/Garde Agri/Comm	Resident	
1,3-dichloropropene	13,648,857								13,648,857
Methyl bromide	9,125,664	4,237		2,533			829		9,133,263
Chloropicrin	2,489,572								2,489,572
Propargite		1,729,387							1,729,387
Molinate		1,674,942							1,674,942
Ziram		914,215							914,215
Permethrin		778,435							778,435
Chlorpyrifos		774,848		100	3			94	775,045
Tributylphosphorotribromide		749,282							749,282
Carbaryl		732,303					1,349	40	733,692
Maneb		701,273							701,273
Azinphos-methyl		542,419							542,419
MCPA, dimethylamine salt		500,755				9	699		500,755
Trifluralin		472,318							473,026
Profenofos		450,102							450,102
Endosulfan		444,431							444,431
Chlorothal-dimethyl		436,446					99		436,545
Methidathion		411,038							411,038
Thiobencarb		404,510							404,510
Malathion		361,432							361,432
Captan		348,632							348,632
2,4-D, dimethylamine salt		312,079	44		4,937				317,060
Ethionon		294,006							294,006
Glyphosate, isopropylamine salt		277,904							283,075
Diazinon		281,128	5,171	60			366		281,554
Acetate		280,486							280,486
Carbofuran		269,910				371			269,910
Dicofol		258,458					41		258,499
Methamidophos		251,427							251,427
Aldicarb		242,402				349			242,751
Mephor		229,738							229,738
Chlorothalonil		225,847							226,367
Naled		225,642	39		520				225,681
Melam-sodium	214,590								214,590
Diuron		200,967							200,967
Pendimethalin		191,829							191,829
Methyl parathion		183,241							183,241

TABLE A-8. (continued)  
Pesticide Use

Active Ingredient	Soil Fumigation	Agricultural	Non-Crop	Industrial	Turf Areas	Nursery	Home-Garden	Agri/Comm	Resident	Total
Formetanate hydrochloride		180,227								180,227
Cyazotol		167,751								167,751
Beetazone, sodium salt		165,770								165,770
Gibberellins		161,181								161,181
Sodium cacodylate		160,174	257							160,431
Dichloras		145,441								145,441
Phorate		140,774								140,774
Disulfoton	2,563	130,337								132,700
Permethrin		127,401								127,401
Sinazifos		124,643	22							124,665
Hydrogen cyanamide		121,485								121,485
Phosmet		117,729								117,729
Oryzalin		113,593				898				114,491
Iperdione		102,976				1,743				104,719
Phenitrothion		94,301								94,301
Bromoxynil octanoate		87,429		3,772	27					91,228
Oxyfluorfen		89,903								89,903
Propoxams		78,022								78,022
Folpet		77,146								77,146
Monocrotophos		74,797				13				74,810
Hezazone		73,464								73,464
Propafl		70,929								70,929
2,4-D, alltrans-isomer salt		69,153								69,153
Fenamiphos		67,756							413	68,169
Thiophanate-methyl		64,832								64,832
Dichlorop-methyl		60,517								60,517
Napropamide		57,139				536				57,675
Thiometon		52,673	50,210			3				102,883
Acrolein		45,949								45,949
Alectol		451								451
Dichloropropene-dichloropropene	44,484	43,616	811							89,911
2,4-D, butoxyethanol ester		42,562								42,562
Sulprofos		41,658								41,658
Ethion		41,271								41,271
Perbutatin-oxide		40,933								40,933
4(2,4-DB), dimethylamine salt		40,289								40,289
Bosulide										

TABLE A-8. (continued)

## Pesticide Use

Active Ingredient	Soil Fumigation	Agricultural	Non-Crop	Industrial	Turf Areas	Nursery	HomeGarde	AgriComm	Resident	Total
Phosphamidon		39,764								39,764
Diquat dibromide		39,705	52							39,757
Prometryn	143	38,374								38,517
Malic hydrazide		37,885								37,885
Foscofen		36,426								36,426
EPYC		35,928								35,928
Anilazine		35,216								35,216
Oxamyl		32,993								32,993
Propham		32,553								32,553
MSMA		32,046	489							32,535
PCNB	2,363	27,902								30,265
Bromacil		30,251	1							30,252
Beesfin		28,965			100					29,065
Cyfluthrin		28,483								28,483
Caustic acid		27,280	32							27,312
2,4-D, 2-ethylhexyl ester		17,561	9,659							27,220
Diethanol-ethyl		26,848								26,848
Chlorobenzilate		24,910								24,910
Metolachlor		22,264								22,264
Vinlozolin		21,473				443				21,916
Dicamba, dimethylamine salt		21,240	16		502					21,758
Atrazine		21,492								21,492
Captafol		20,487								20,487
2,4-D, diethanolamine salt		20,024								20,024
Chloroxuron		19,904								19,904
Fen-sulfathion		19,337								19,337
Demeton		15,526								15,526
2,4-D, triethylamine salt		15,288								15,288
2,4-D		12,071								12,071
2,4-D, n-octyl, 1,3-propylene-diamine salt		11,456								11,456
Metribuzin		10,602								10,602
Bromoxynil, butyric acid ester		7,671								7,671
Total	25,528,026	20,240,566	66,803	6,465	6,089	4,365	2,554	869	507	45,856,244
										0
										0

TABLE A-9. COMPARISON OF AERIAL AND GROUND APPLICATION RATES  
BY ACTIVE INGREDIENT

Active Ingredient	Actives and Solvents		Total	Application Method			Average Application Rate (lbs/acre)	
	Lbs Active	Lbs Solvent		Ground	Air	Other	Ground	Air
1,3-dichloropropene	13,848,857		13,848,857	13,133,239	143,284	372,336	79.5	83.6
Methyl bromide	9,133,281		9,133,281	8,889,506	14,792	228,877	126.8	23.5
Chloropicrin	2,489,572		2,489,572	2,466,112	8,589	14,868	43.7	37.9
Propargile	1,728,387	390,235	2,119,022	636,289	1,186,824	6,272	1.8	1.7
Chlorpyrifos	776,042	915,075	1,690,117	242,004	521,815	11,334	2.1	0.7
Malathion	1,874,942		1,874,942	63,631	1,572,944	38,375	6.5	5.8
Methidathion	411,038	1,138,777	1,549,815	313,138	85,049	2,850	1.8	0.5
Tributylphosphorotriphosphate	749,282	281,945	1,030,927	278,367	465,828	7,287	1.8	1.5
Endosulfan	444,433	528,849	971,082	195,463	246,906	2,064	1.1	0.9
Maneb	701,273	225,458	926,731	332,558	387,980	755	1.8	2.3
Ziram	914,215		914,215	162,739	742,883	8,783	2.9	7.2
Parathion	778,435	105,184	883,619	825,652	143,131	9,851	1.9	0.5
Carbaryl	733,602	42,115	775,707	477,605	252,331	3,668	4.6	2.0
Azinphos-methyl	542,418	107,358	649,777	377,948	180,817	3,915	1.3	1.4
Proflonol	450,102	183,859	633,961	8,912	435,349	5,942	0.9	1.0
Trifluralin	473,025	64,957	537,982	178,178	293,813	1,039	0.9	1.5
Dicofol	258,498	253,843	522,140	209,929	47,288	1,281	1.0	0.8
MCPA, dimethylamine salt	500,755		500,755	134,181	365,672	921	2.8	1.0
Chlorthal-dimethyl	436,544		436,544	352,141	82,798	1,808	4.3	7.9
Malethion	381,432	44,368	425,800	24,780	336,140	498	2.1	1.4
Thiobencarb	404,510		404,510	403,906		604		3.9
Ethephon	294,006	72,224	366,230	63,464	228,222	2,301	0.9	0.9
Captan	348,632		348,632	152,972	192,023	3,639	1.9	3.2
Diazinon	281,551	50,310	331,861	88,334	211,884	1,359	0.9	0.8
Pendimethalin	191,828	138,440	330,269	102,589	88,041	1,219	1.2	1.2
Chlorothalonil	226,368	96,182	322,548	87,885	156,250	234	1.5	1.3
2,4-D, dimethylamine salt	317,059		317,059	158,445	154,225	4,391	0.9	0.8
Merphos	229,738	86,356	316,094	52,395	176,670	674	1.9	2.2
Naled	225,681	68,252	293,933	73,522	149,462	2,698	2.0	0.9
Oxyfluorfen	89,903	194,328	284,229	76,033	13,491	378	0.6	0.2
Glyphosate, isopropylamine salt	283,074		283,074	188,084	93,450	1,543	0.8	0.5
Acephate	280,857		280,857	101,374	154,724	24,759	0.9	0.8
Carbuhar	269,910		269,910	117,228	142,905	9,777	1.4	0.5
Methamidophos	251,427		251,427	45,395	204,537	1,494	0.8	0.7
Aldicarb	242,750		242,750	235,389	453	6,909	1.1	1.1
Phosalune	94,301	142,114	236,415	52,746	40,651	904	2.1	2.3

TABLE A-9. (Continued)

Active Ingredient	Actives and Solvents		Total	Application Method			Average Application Rate (lb/acre)	
	Lbs Active	Lbs Solvent		Ground	Air	Other	Ground	Air
Methyl parathion	193,241	51,762	235,003	19,432	163,478	329	0.6	0.6
Malam-sodium	214,560		214,560	204,390		10,190	44.3	—
Duron	200,967		200,967	129,679	70,214	1,075	1.4	1.9
Formetanate hydrochloride	180,227		180,227	102,114	78,765	1,348	1.4	0.9
Cyazoline	167,761		167,761	146,907	18,898	1,948	1.6	2.8
Bentazon, sodium salt	165,770		165,770	11,309	153,840	621	1.9	1.2
Gliberelline	161,181		161,181	161,155	21	6	2.7	—
Sodium cacodylate	160,431		160,431	43,805	114,416	2,211	0.7	0.7
Pebulate	127,401	26,501	153,902	127,251		150	17.5	—
Dichloran	145,441		145,441	140,909	4,173	360	3.1	1.9
Deutolton	132,700	8,747	141,447	79,613	51,578	1,508	0.9	0.9
Phorate	140,774		140,774	82,431	47,528	616	0.8	1.2
Simazine	124,666		124,666	122,634	706	836	1.1	1.5
Monocrotophos	74,809	46,859	121,668	33,782	40,318	712	0.7	0.7
Phosmet	117,729		117,729	29,020	87,766	644	2.0	0.8
Oryzalin	114,491		114,491	110,303	2,981	1,208	2.0	3.9
Bromoxynil octanoate	91,226	15,146	106,372	15,259	75,662	277	0.5	0.6
Iprodione	104,719		104,719	45,736	58,264	720	0.8	0.5
Napropamide	57,676	40,733	98,409	56,439	888	348	1.9	3.0
Bensulfide	40,289	40,289	80,578	29,240	10,900	60	2.4	3.8
Propyzamide	78,022		78,022	64,054	13,767	183	0.8	1.1
Folpet	77,146		77,146	22,390	54,751	36	1.2	1.1
Hexazinone	73,464		73,464	37,090	35,543	832	0.7	0.8
Propanil	70,929		70,929	2,490	68,356	134	1.4	4.1
2,4-D, sikanolamine salt	69,153		69,153	40,427	28,271	454	1.1	1.0
Fenamiphos	68,169		68,169	39,066	45	29,058	2.2	1.1
Fonolox	36,426	31,564	67,990	35,980	278	170	0.9	0.9
Thiophanate-methyl	64,032		64,032	13,098	50,465	469	0.9	0.9
Diclofop-methyl	60,517		60,517	8,840	51,499	178	0.6	0.8
Ethion	41,658	18,036	59,694	18,020	23,441	198	1.1	1.1
Diethyl-ethyl	26,848	30,198	57,044	25,008	1,462	378	2.8	3.7
Triadimefon	52,676		52,676	41,440	11,042	194	0.2	0.1
Sulprofos	42,562	8,924	51,486	622	41,792	148	0.8	1.2
2,4-D, butoxyethanol ester	44,427	6,274	50,701	13,960	30,173	293	0.7	1.1
Chlorobenzilate	24,910	25,457	50,367	22,385	2,091	433	0.7	1.1
Acrolein	50,210		50,210	15,662		34,548	2.1	—

TABLE A-9. (Continued)

Active Ingredient	Actives and Solvents		Total	Application Method		Average Application Rate (lbs/acre)	
	Lbs Active	Lbs Solvent		Ground	Air	Ground	Air
Alachlor	45,049		45,049	44,900	80	2.8	3.2
Dichloropropene-dichloropropene	44,934		44,934	42,478	1,772	118.4	8.6
Phosphamidon	39,794	4,382	44,156	31,038	8,630	4.0	0.9
Fenbutalin-oxide	41,271		41,271	38,712	4,280	1.0	0.9
4(2,4-D6), dimethylamine salt	40,833		40,833	8,242	32,631	1.1	1.5
Diquat dibromide	39,767		39,767	8,098	33,647	1.0	0.8
EPTC	36,938	2,717	38,645	35,397	227	2.8	2.7
Prometryn	38,617		38,617	36,370	3,098	1.3	1.4
Maleic hydrazide	37,885		37,885	325	37,561	2.7	3.7
Anilazine	35,218		35,218	11,378	23,845	1.4	1.8
Oxamyl	32,994		32,994	12,112	20,395	0.5	0.6
Propham	32,653		32,653	8,635	25,917	2.8	4.7
MSMA	32,638		32,638	18,309	16,042	2.0	2.0
Bromacil	30,271		30,271	30,014	6		
PCNB	30,265		30,265	29,950	253	0.6	1.9
Benflin	29,065		29,065	24,246	4,264	1.1	1.4
Cyhexalin	28,483		28,483	28,484	1,809	0.8	1.3
Vinclozolin	21,915	5,583	27,498	17,034	4,871	0.7	0.8
Cacodylic acid	27,312		27,312	7,458	19,479	0.2	0.1
2,4-D, 2-ethylhexyl ester	27,220		27,220	2,508	24,713	0.8	2.8
Metolachlor	22,284		22,284	7,485	14,760	2.2	2.6
Dicamba, dimethylamine salt	21,757		21,757	13,744	7,915	0.3	0.2
Atrazine	21,492		21,492	4,744	16,749	1.3	2.1
Captaol	20,487		20,487	4,249	15,998	1.9	2.8
2,4-D, diethanolamine salt	20,043		20,043	6,117	13,922	1.1	0.8
Chloroxuron	19,904		19,904	19,874	231	1.6	1.3
Fenitrothion	19,337		19,337	19,337			
Demeton	15,528		15,528	12,931	2,592	0.5	0.4
2,4-D, n-octyl 1,3-propylenediamine salt	11,458	3,982	15,438	3,372	8,084	0.5	0.7
2,4-D, triethylamine salt	15,288		15,288	14,399	531	0.8	0.7
2,4-D	12,071	2,708	14,777	5,501	6,500	0.2	0.4
Metribuzin	10,602		10,602	3,472	7,085	0.5	0.6
Bromoxynil, butyric acid ester	7,671		7,671	3,468	4,205	0.3	0.3

TABLE A-10. PESTICIDE USAGE BY COUNTY

County	Total
Fresno	5,650,586
Kern	5,521,522
Monterey	3,943,322
Santa Barbara	3,086,341
San Joaquin	2,768,163
Merced	2,532,019
Imperial	2,264,743
Tulare	2,207,021
Ventura	1,840,200
Stanislaus	1,793,864
Kings	1,533,678
Sutter	1,230,876
Riverside	1,189,470
Santa Cruz	969,904
San Luis Obispo	958,220
Butte	824,288
Colusa	797,489
Madera	676,935
Yolo	671,154
San Diego	613,624
Glenn	611,179
Orange	510,813
Solano	370,334
Sacramento	326,653
Yuba	317,404
Sonoma	232,543
Shasta	227,364
Lassen	218,771
Napa	208,091
Siskiyou	156,091
Modoc	131,509
Del Norte	123,156
Tehama	121,453
Santa Clara	120,586
San Penito	109,292
San Bernardino	87,556
Los Angeles	86,588
San Mateo	77,411
Placer	70,339
Humboldt	57,048
Contra Costa	30,691
Alameda	25,221
El Dorado	24,365
Lake	23,870
Plumas	17,338
Mendocino	13,335
Calaveras	9,745
Mono	9,471
Alpine	4,810
Nevada	4,548
Marin	4,293
Amador	3,301
Sierra	1,176
Invo	1,063

TABLE A-10. (Continued)

<u>County</u>	<u>Total</u>
Trinity	955
Tuolumna	658
San Francisco	448
Mariposa	200
Total	45,413,088



TABLE A-11. 1987 PESTICIDE USAGE BY COMMODITY (LB ACTIVE)

Commodity	Total
Strawberries	6,379,891
Cotton	4,942,391
Almonds	3,030,404
Rice	2,758,342
Carrot	2,479,263
Tomato	2,379,459
Sugarbeet	1,845,839
Grapes	1,748,177
Open Land	1,616,960
Alfalfa	1,519,930
Broccoli	1,458,534
Lettuce (head)	960,544
Fallow Farm Land	955,197
Orange	820,624
Sweet Potato	767,679
Potato	756,243
Roses	708,181
Cauliflower	700,427
Peppers (bell)	687,351
Peach	591,788
Turf	573,288
Melons	564,979
Wheat	478,299
Beans	454,789
Walnut	435,767
Corn	419,384
Ornamentals	409,045
Brussels Sprouts	367,066
Flowers	335,992
Onions	303,479
Celery	286,075
Soil Fumigation	256,538
Lemon	241,883
Prune	234,284
Apple	200,198
Bulbs	142,187
Cabbage	142,004
Watermelons	137,893
Non-Agricultural Areas	127,668
Plum	125,052
Asparagus	124,770
Pistachio	122,550
Nectarines	121,324
Orchard Floors	118,084
Barley	112,107
Citrus	104,461
Lettuce (leaf)	103,734
Safflower	75,227

TABLE A-11. (Continued)

Commodity	Total
Oats	74,877
Parsley	74,571
Berries, other	64,647
Apricot	62,765
Pear	59,103
Artichoke	58,226
Cherries	57,834
Olives	57,730
Squash	54,020
Water Areas	53,575
Pasture/Rangeland	45,314
Spinach	43,762
Grapefruit	36,365
Garlic	35,317
Forest/Timberland	34,703
Conifers	32,473
Pumpkins	27,555
Cucumber	25,139
Avocado	23,806
Clover	23,443
Figs	14,381
Beets	12,369
Deciduous Ornamental Trees	11,173
Rutabaga	11,052
Kiwi	10,749
Eggplant	10,174
Date	9,834
Miscellaneous	9,233
Peas	8,117
Nuts, other	7,310
Sorghum	7,310
Parsnip	7,154
Poultry Buildings	6,148
Sunflower	6,128
Food Processing Plants	5,310
Vegetable Seed	5,076
Peppers (chili)	4,969
Kale	4,063
Chives	3,600
Grain	2,886
Tangerine/Tangelo	2,841
Sudangrass	2,749
Forage, hay & silage	2,689
Dried Fruit	2,586
Turnip	2,583
Swiss Chard	2,202
Pecan	2,136
Mustard	1,286

TABLE A-11. (Continued)

Commodity	Total
Pomegranate	1,203
Alfalfa Sprouts	1,193
Radish	1,131
Greenhouse Fumigation	1,046
Wild Rice	988
Anise	945
Chicken	776
Mushrooms	756
Industrial Areas	740
Evergreen Trees	704
Quince	608
Collard	522
Oriental Vegetables	485
Shrubs	423
Citrus, other	339
Leeks	311
Hemp	286
Small fruits	240
Sweet Basil	220
Limes	200
Rye	172
Nuts	150
Livestock Buildings	139
Weed Control	135
Vetch	124
Structural Control	103
Okra	99
Sub-tropical fruits, other	59
Kohlrabi	58
Cattle, Beef, & Dairy	57
Triticale	49
Endive	38
Soybean	24
Residential areas	21
Ryegrass	7
Recreational Areas-Parks	4
Rights of Way	4
Flax	3



TABLE A-12. (continued)

Active Ingredient	January	February	March	April	May	June	July	August	September	October	November	December	Total
Crysoline	14,204	14,107	17,248	2,085	82	128	330	76	1,574	3,123	30,105	33,045	114,489
Ipridione	79	33,821	30,374	3,106	13,255	4,554	2,740	6,281	308	305	444	102	104,722
Phenothiazine	373	460	382	22,542	22,946	30,753	8,116	8,151	308	308	444	160	94,300
Benzothiazyl disulfide	8,060	30,466	21,532	5,608	700	294	72	70	200	573	3,996	8,416	91,228
Chlorfenvinphos	9,139	4,753	2,306	1,807	508	1,706	624	94	108	5,085	20,745	32,482	60,907
Propoxuron	7,804	6,640	5,101	4,666	4,005	6,905	6,650	11,005	5,157	4,400	7,326	7,326	70,085
Folpet	621	1,066	3,743	5,596	15,230	7,665	7,665	6,601	14,812	7,873	2,572	648	71,153
Monocrotophos	6	8	12	2,010	21,837	14,975	13,465	17,427	4,779	37	13	19	74,000
Hexamethylenetetramine	20,323	6,774	4,146	3,067	2,205	33,437	14,297	524	753	11,456	3,853	22,300	71,466
Propoxur	2,380	9,250	10,700	5,512	6,145	7,850	5,313	1,142	966	4,035	4,182	1,433	70,059
2,4-D, dichloromethyl salt	454	1,512	14,414	17,300	6,527	4,500	705	1,850	7,754	6,790	3,460	344	60,155
Phenolphthalein	150	32,230	22,606	1,076	1,270	1,315	1,100	1,424	779	206	453	235	64,033
Thiophan-methyl	1,874	37,308	12,062	3,065	320	19	414	415	526	2,391	4,630	13,841	60,517
Dieldrin-methyl	9,000	6,641	6,641	5,660	2,310	11,020	4,435	3,850	1,835	310	34	80	57,679
Napropamide	64	270	226	9,591	20,921	11,020	121	415	526	2,391	4,630	13,841	52,679
Acetaminophen	907	3,411	2,566	2,756	7,000	11,250	13,107	6,553	1,607	700	34	80	50,110
Alachlor	116	172	1,381	1,437	17,674	8,291	3,573	6,553	1,607	700	34	80	43,048
2,4-D, isopropyl ester	2,597	10,771	14,210	8,704	1,957	2,010	600	400	15,616	4,121	4,608	315	44,934
Suberone	1,214	2,439	2,741	1,601	3,774	4,444	14,221	22,071	4,700	1,005	317	315	44,934
Bifenox	129	223	460	3,300	16,207	7,231	8,464	6,070	4,300	1,321	427	57	41,659
2,4-D, isopropyl ester	2,094	4,072	5,370	2,432	643	1,430	340	3,045	1,340	144	427	57	41,659
2,4-D, isopropyl ester	5,707	3,125	3,145	756	370	534	2,401	4,100	10,206	2,824	2,720	1,072	40,033
Phosphamidon	34	167	135	1,004	1,005	8,361	8,752	17,718	472	145	30	22	40,200
Disposal dithionite	91	160	224	297	243	232	1,285	27,464	7,306	720	1,400	57	30,757
Phenoxypyrazole	1,071	3,045	6,011	9,000	1,004	4,370	3,004	2,000	2,519	1,530	900	400	30,516
Isobutyl pyridine	559	1,266	3,600	13,100	14,252	5,300	1,004	33,701	2,522	104	212	100	37,085
Permethrin	2,654	2,400	4,105	6,670	8,421	4,250	1,400	3,070	174	104	212	100	36,030
SP7C	2,222	1,804	3,900	1,371	1,906	1,673	2,555	1,704	2,273	2,001	6,500	670	35,000
Adjuvant	942	312	708	1,531	2,720	2,255	1,103	4,750	8,082	7,717	1,190	733	32,217
Chlorpyrifos	5,740	3,255	7,000	90	1,120	2,255	236	416	2,916	3,015	4,004	3,697	32,907
Metolachlor	6	160	327	900	7,100	5,974	3,404	5,010	6,776	2,078	346	8	32,530
Permethrin	2,370	5,625	3,640	1,270	630	240	91	57	220	641	5,071	10,191	30,270
PCNB	290	2,240	3,554	21,070	2,155	1,105	544	3,497	60	375	330	485	30,367
Benlate	565	128	307	600	1,456	1,456	2,214	3,497	6,466	6,257	2,911	2,107	20,067
Cyfluthrin	654	1,374	4,207	5,175	10,020	6,251	6	9	4	10,365	1,322	2,107	20,067
Carbaryl and	33	300	1,251	10,454	826	11,020	67	94	14	10,365	1,322	2,107	20,067
2,4-D, 2-ethylhexyl ester	2,425	1,210	663	3,576	7,664	3,306	1,291	643	997	1,576	1,532	1,647	27,221
Dichlorvos	37	63	532	3,607	2,270	1,671	1,300	3,814	4,112	4,600	2,174	407	24,000
Chlorobenzilate	376	71	127	2,303	2,120	5,362	405	166	1,300	2,031	5,742	2,673	22,364
Verdine	1,124	2,250	4,005	2,309	2,354	1,904	1,904	2,360	1,300	1,240	325	8	21,000
Diazinon, dimethylphosphate salt	1,000	4,427	3,346	2,575	2,340	4,595	1,804	440	1,151	137	291	559	21,750
Azinphos	19	200	1,371	1,107	11,300	4,402	2,405	4,056	1,151	137	92	59	21,000
Captafol	240	240	713	1,317	722	4,375	5,304	4,056	1,543	2,252	194	500	20,400
2,4-D, dichloromethyl salt	630	10,675	3,713	1,317	722	770	530	350	70	371	303	500	20,400

TABLE A-12. (continued)

Active Ingredient	January	February	March	April	May	June	July	August	September	October	November	December	Total
Chloramphenicol	300	514	1,197	3,432	3,431	2,135	3,652	3,357	2,044	146	167	84	19,907
Penicillin	749	840	3,252	4,744	2,124	9,072	145						19,337
Doxycycline	829	1,540	843	1,886	1,233	1,999	2,800	2,726	2,107	934	82	187	15,526
2,4-D, trisophtaline salt	314	4,031	3,435	3,244	2,129	1,442	1,405	399	481	366	383	146	15,299
2,4-D	86	5,085	4,376	1,840	673	587	456	153	94	249	90	94	12,071
2,4-D, o-crotyl 1,3-propylenediamine salt	199	645	4,468	778	332	113	225	45		180			11,456
Methidathion	643	1,443	3,716	1,300	217	2,677	2,378		146	1,180	1,124	1,449	18,664
Bromopropyl butyric acid ester					48		1		13		310	257	7,671
Total	1,008,942	2,454,489	3,778,158	3,891,447	4,635,714	3,221,139	4,568,452	4,774,164	5,154,177	4,798,578	3,247,886	3,483,867	45,856,446

**APPENDIX B**  
**RESOURCES FOR THE FUTURE DATA BASE**





## APPENDIX B. RESOURCES FOR THE FUTURE DATA BASE

### B.1 DATA BASE CONTENT

Two dBase data bases were obtained from Resources for the Future (RFF) to estimate pesticide usage information summarized in this document. The herbicide active ingredient (AI) use information was obtained from the National Pesticide Use Inventory compiled by RFF.<sup>1</sup> The insecticide information also came from RFF. Resources for the Future gathers information on pesticide use and compiles the information in a comprehensive data base format. Funding for the RFF studies comes from the Environmental Protection Agency (EPA), the U.S. Department of Agriculture (USDA), the National Oceanic and Atmospheric Administration (NOAA) and several pesticide manufacturers. The RFF data bases were created based on pesticide usage estimates calculated using two coefficients: the percent of acres that are treated and the average annual application rate per treated acre.<sup>1</sup> These coefficients are typically provided in terms of Statewide average use for a particular AI and crop combination for a year typical of the 1980's (1987-1989 for herbicides and 1982-1984 for insecticides). Multiplying these coefficients by estimates of the number of planted crop acres reported in the 1982 Census of Agriculture for insecticides and the 1987 Census of Agriculture for herbicides provides estimates of the number of acres that are treated. The number of treated acres is multiplied by the application rate per acre to estimate the total poundage of AI used on the crop in a county.

Information on herbicides is available on the county level which allows analysis of herbicide use in ozone nonattainment areas. Insecticide and fungicide data were available only on the

State level. No information on other types of pesticides was compiled for these data bases.

The file names and structures of each data base are presented in Attachment 1. In general, a data base file is comprised of records, and one record consists of one set of the fields outlined in the data base structure. Data may be organized by any field or any combination of fields. The two data bases contain information on the major insecticide AI's and herbicide AI's in terms of use in the United States. The two pesticide classes, insecticides and herbicides, constituted over 80 percent of the total U.S. pesticide market in 1990.<sup>2</sup> Therefore, it is assumed that these data bases cover the majority of the pesticide market in terms of pesticide classes and the number of AI's. Based on 80 percent of the market, it is assumed that herbicides and insecticides will constitute the major sources of volatile organic compound (VOC) emissions from the application of agricultural pesticides. The use of the term "total pesticides" refers to herbicides plus insecticides.

The first data base contains insecticide use data from 1982 to 1984 for 16 AI's. Information is organized by insecticide, by crop, and by State. Other information provided in fields include: acres of crop grown (or harvested) according to the 1982 Census of Agriculture, percent crop treated, pounds of AI per acre treated per year, pounds of AI used per year, and number of acres treated. This data base file contains 2,042 records of information.

The second data base contains use information from 1987 on 94 herbicides organized by herbicide, five-digit Federal Information Processing Standard (FIPS) code, and crop code. A five-digit FIPS code is a numerical code; the first two numerals identify the State, and the last three numerals identify the county. The crop code is simply a three-digit code that corresponds to one of 84 crop types used in the data base. Other types of information provided in fields include harvested crop acreage by county, percent of acres treated with the herbicide, average annual use of AI per treated acre or rate of application

(calculated by RFF from pounds AI/acre/year), total acres treated in a given county (calculated by RFF from total acres x percent treated x 0.01), and total pounds of AI used on a crop in the county (calculated by RFF from: acres treated x rate). The herbicide data base contains 191,000 records of information.

For purposes of analysis, MRI appended the FIP's code field to the herbicide data base to identify pesticide use in counties designated as whole or partial ozone nonattainment areas. This was done by matching FIPS codes with the 1990 Clean Air Act Amendment information on county ozone nonattainment status.

Pesticide usage information comes from the field "pounds of AI used" in each data base. Resources for the Future estimated the pounds of AI used from two coefficients: the percent of acres that are treated and the average annual application rate per treated acre. State-level usage coefficients were obtained from surveys published for individual States, Extension Service personnel, and USDA usage surveys.<sup>1</sup> County-level usage coefficients were calculated from State average coefficients, assuming a uniform application rate within a State.<sup>1</sup> Then the State- or county-level coefficients were multiplied by the corresponding number of planted crop acres to estimate the total State or county pounds of AI used on a crop.<sup>1</sup> Pesticide usage is calculated by totalling the field "pounds of AI" according to other factor(s) such as county, State, crop, etc.

## B.2 PESTICIDE USAGE AND SOLVENT EMISSIONS TABLES

Tables highlighting different aspects of the available pesticide use information were constructed. Total pesticide (herbicide plus insecticide) usage nationwide and in ozone nonattainment areas nationwide is presented in Table B-1. The data in this table were taken from both the herbicide and insecticide data bases.

The insecticide data base was indexed by State and then by insecticide. The pounds of AI used were totalled for each AI across all crops for each State and then totalled across all AI's for each State (Table B-1) to obtain nationwide insecticide usage. Total usage of an AI nationwide was also calculated and

TABLE B-1. AGRICULTURAL PESTICIDE USAGE IN POUNDS OF ACTIVE INGREDIENT USED

State	Herbicides		Insecticides		Total	
	State use	Nonattainment areas	State use	Nonattainment areas*	State use	Nonattainment areas
Alabama	4,366,624	35,688	6,264,874	51,202	10,631,498	86,890
Arizona	2,363,655	502,452	596,635	126,829	2,960,290	629,281
Alaska	0	0	0	0	0	0
Arkansas	13,713,417	0	3,816,681	0	17,530,098	0
California	14,132,412	12,204,388	15,122,664	13,059,544	29,255,076	25,263,932
Colorado	5,619,988	138,777	255,214	6,302	5,875,202	145,079
Connecticut	177,637	177,637	75,482	75,482	253,119	253,119
Delaware	1,223,795	1,223,795	340,595	340,595	1,564,390	1,564,390
Florida	8,130,340	2,849,395	6,501,544	2,278,560	14,631,884	5,127,955
Georgia	7,346,790	72,624	11,902,828	117,661	19,249,618	190,285
Hawaii	0	0	0	0	0	0
Idaho	6,019,919	0	1,577,745	0	7,597,664	0
Illinois	45,406,451	3,818,865	969,265	81,519	46,375,716	3,900,384
Indiana	24,884,723	1,566,364	595,278	37,470	25,480,001	1,603,834
Iowa	48,681,610	0	669,499	0	49,351,109	0
Kansas	17,467,606	117,203	994,274	6,671	18,461,880	123,874
Kentucky	8,245,756	902,268	1,117,072	122,232	9,362,828	1,024,500
Louisiana	12,026,887	1,396,738	4,767,205	553,638	16,794,092	1,950,376
Maine	382,492	116,568	256,476	78,163	638,968	194,731
Maryland	3,411,723	1,863,927	532,157	290,733	3,943,880	2,154,660
Massachusetts	292,176	292,176	150,230	150,230	442,406	442,406
Michigan	12,622,026	11,198,487	1,568,607	1,391,696	14,190,633	12,590,183
Minnesota	31,630,190	0	833,135	0	32,463,325	0
Mississippi	9,511,970	0	4,397,909	0	13,909,879	0
Missouri	16,740,190	738,690	2,960,957	130,657	19,701,147	869,347
Montana	3,744,821	0	393,184	0	4,138,005	0
Nebraska	22,229,785	0	935,844	0	23,165,629	0
Nevada	121,540	5,166	2,512	107	124,052	5,273
New Hampshire	32,061	22,410	1,880	1,314	33,941	23,724

TABLE B-1. CONT.

State	Herbicides		Insecticides		Total	
	State use	Nonattainment areas	State use	Nonattainment areas*	State use	Nonattainment areas
New Jersey	931,348	931,348	507,193	507,193	1,438,541	1,438,541
New Mexico	3,067,816	0	167,590	0	3,235,406	0
New York	6,518,147	1,170,278	2,080,758	373,582	8,598,905	1,543,860
North Carolina	7,816,672	279,316	4,954,204	177,030	12,770,876	456,346
North Dakota	11,464,667	0	827,702	0	12,292,369	0
Ohio	19,137,324	5,130,793	873,975	234,316	20,011,299	5,365,109
Oklahoma	4,432,246	0	1,006,328	0	5,438,574	0
Oregon	3,416,713	753,282	765,128	168,688	4,181,841	921,970
Pennsylvania	5,894,544	4,670,042	965,493	764,926	6,860,037	5,434,968
Rhode Island	20,346	20,346	5,415	5,415	25,761	25,761
South Carolina	3,375,463	19,466	5,706,296	32,908	9,081,759	52,374
South Dakota	12,842,621	0	506,835	0	13,349,456	0
Tennessee	6,282,383	337,230	1,779,487	95,521	8,061,870	432,751
Texas	27,207,216	2,066,466	4,589,887	348,615	31,797,103	2,415,081
Utah	2,065,275	32,717	23,376	370	2,088,651	33,087
Vermont	463,911	0	16,833	0	480,744	0
Virginia	4,309,911	658,789	2,013,765	307,813	6,323,676	966,602
Washington	3,569,985	60,779	1,302,431	22,174	4,872,416	82,953
West Virginia	486,421	42,379	117,011	10,194	603,432	52,573
Wisconsin	11,014,385	1,494,125	519,403	70,458	11,533,788	1,564,583
Wyoming	2,771,259	0	78,444	0	2,849,703	0
Nationwide	457,615,237	56,910,974	96,407,300	22,019,811	554,022,537	78,930,785

\* Estimated

the usages from all of the AI's ranked in descending order (Attachment 2). Since the insecticide data base did not contain county-level information, ozone nonattainment information was estimated from the herbicide ozone nonattainment data. For each State, the percent of total herbicide use in ozone nonattainment areas was calculated and this percentage applied to the total insecticide use in order to approximate the insecticide use in ozone nonattainment areas.

The herbicide data base was manipulated in a slightly different manner. In order to extract information for herbicide use in ozone nonattainment areas, both county- and state-level data were used. The original data base was obtained from RFF on nine diskettes organized primarily by herbicide and crop. For our purposes, the diskettes were combined on a Bernoulli disk to allow access to information by State and county organization. Nationwide (Table B-1) and county-level (Attachment 3) herbicide use data for ozone nonattainment areas were taken from this data base. Use rankings for herbicides in the data base nationwide and in ozone nonattainment areas are provided in Attachments 4 and 5, respectively.

The data base was then divided by State into smaller, more easily handled pieces. The State data bases were indexed by herbicide, and the field "pounds of AI used" was totalled across crops and county for each AI and for ozone nonattainment areas only on the State level (Table B-1).

Table B-2 presents the solvent emissions calculated for each state nationwide and in ozone nonattainment areas. These emissions are based only on the approximated solvent content of the following herbicide and insecticide AI's: methyl parathion, ethoprop, diazinon, oxamyl, alachlor, metolachlor, 2,4-D, butylate, pendimethalin, propanil, propachlor and bromoxynil. The method used to calculate nonaqueous solvent emissions is described in section 4.3. The contribution of insecticides to solvent emissions in ozone nonattainment areas was estimated based on the ratio of herbicide contributions in ozone nonattainment areas and nationwide.

TABLE B-2. ESTIMATED AGRICULTURAL NONAQUEOUS SOLVENT EMISSIONS BY STATE

State	Solvent emissions from herbicides, pounds		Solvent emissions from insecticides, pounds		Total solvent emissions, pounds	
	State	Nonattainment Areas	State	Nonattainment Areas*	State	Nonattainment Areas
Alabama	750,063	4,625	187,904	1,159	937,967	5,784
Arizona	685,410	128,845	111,798	21,016	797,208	149,861
Alaska	0	0	0	0	0	0
Arkansas	8,856,157	0	97,579	0	8,953,736	0
California	1,411,646	1,288,599	483,793	441,623	1,895,439	1,730,222
Colorado	995,997	28,095	9,882	279	1,005,879	28,374
Connecticut	14,634	14,634	12,705	12,705	27,339	27,339
Delaware	211,909	211,909	4,538	4,538	216,447	216,447
Florida	524,241	36,191	149,646	10,331	673,887	46,522
Georgia	1,784,781	19,897	666,025	7,425	2,450,806	27,322
Hawaii	0	0	0	0	0	0
Idaho	896,373	0	107,769	0	1,004,142	0
Illinois	8,053,182	671,880	69,757	5,820	8,122,939	677,700
Indiana	4,823,417	300,309	13,026	811	4,836,443	301,120
Iowa	7,888,878	0	44,205	0	7,933,083	0
Kansas	2,835,179	20,366	5,393	39	2,840,572	20,405
Kentucky	1,304,466	147,315	12,493	1,411	1,316,959	148,726
Louisiana	2,906,331	300,133	1,470,460	151,852	4,376,791	451,985
Maine	26,714	11,636	19	8	26,733	11,644
Maryland	519,894	255,383	25,501	12,527	545,395	267,910
Massachusetts	24,082	24,082	44,194	44,194	68,276	68,276
Michigan	1,561,390	1,421,331	105,054	95,631	1,666,444	1,516,962
Minnesota	4,595,200	0	13,106	0	4,608,306	0
Mississippi	2,189,022	0	747,815	0	2,936,837	0
Missouri	4,196,934	163,193	103,247	4,015	4,300,181	167,208
Montana	635,794	0	37,602	0	673,396	0
Nebraska	3,636,522	0	58,068	0	3,694,590	0
Nevada	9,755	0	29	0	9,784	0
New Hampshire	4,052	2,805	444	307	4,496	3,112

TABLE B-2. CONT.

State	Solvent emissions from herbicides, pounds		Solvent emissions from insecticides, pounds		Total solvent emissions, pounds	
	State	Nonattainment Areas	State	Nonattainment Areas*	State	Nonattainment Areas
New Jersey	121,539	121,570	35,418	35,427	156,957	156,997
New Mexico	617,259	0	6,738	0	623,997	0
New York	1,084,536	178,684	293,349	48,331	1,377,885	227,015
North Carolina	1,798,590	62,884	275,973	9,649	2,074,563	72,533
North Dakota	1,525,853	0	6,420	0	1,532,273	0
Ohio	3,255,215	854,264	37,902	9,947	3,293,117	864,211
Oklahoma	875,716	0	95,629	0	971,345	0
Oregon	367,311	59,063	53,467	8,597	420,778	67,660
Pennsylvania	888,831	712,317	32,592	26,120	921,423	738,437
Rhode Island	2,821	2,821	32	32	2,853	2,853
South Carolina	539,072	3,652	313,408	2,123	852,480	5,775
South Dakota	2,722,102	0	2,453	0	2,724,555	0
Tennessee	1,079,797	63,490	5,303	312	1,085,100	63,802
Texas	6,216,589	1,012,329	451,630	73,545	6,668,219	1,085,874
Utah	494,084	6,794	2,923	40	497,007	6,834
Vermont	61,005	0	574	0	61,579	0
Virginia	827,149	126,891	138,021	21,173	965,170	148,064
Washington	507,337	8,549	12,202	206	519,539	8,755
West Virginia	44,949	4,015	38,889	3,474	83,838	7,489
Wisconsin	1,306,341	184,081	27,628	3,893	1,333,969	187,974
Wyoming	569,384	0	0	0	569,384	0
Nationwide	86,247,503	8,452,632	6,412,603	1,058,558	92,660,106	9,511,190

\* Estimated



### B.3 PESTICIDE USAGE ESTIMATES

Total pesticide usage estimates for each State as well as nationwide are presented in Table B-1. Data are listed for total pesticide, herbicide, and insecticide use in pounds of AI's used and total pesticide, herbicide, and insecticide use in pounds of AI's used only in ozone nonattainment areas. These data were compiled for each State from both the herbicide and insecticide data bases. The data bases include information only for the contiguous States; therefore, no data are presented for Hawaii and Alaska.

Nationwide, 554 million pounds of herbicide and insecticide AI's were applied to cropland. Herbicides accounted for over 80 percent of the total use (458 million pounds of AI's). Insecticide use amounted to 96 million pounds of AI's. The States with the largest contributions overall to total pesticide use were Iowa, Illinois, Minnesota, Texas, and California. The percent contributions of these States to the nationwide total pesticide use, nationwide total herbicide use, and nationwide total insecticide use are presented in Table B-3.

Of these States, the majority of pesticide use (85 percent or greater) is due to the use of herbicides. Data base information on the top four States indicates that the largest volume of herbicide AI used in each of the States is used primarily for weed control in corn including atrazine, metolachlor, and alachlor. The top three States contributed one percent or less to the nationwide insecticide use. California insecticide use (15 million pounds of AI's), however, accounted for greater than half of the State's pesticide use. This was largely a result of the use of dibromochloropropane (DBCP), which accounted for 65 percent of California's insecticide use. Dibromochloropropane is a soil fumigant used to treat a variety of crops including citrus, berries, grapes, cotton, vegetables, and ornamentals. Its registration was cancelled in 1985. The major soil fumigants listed in the 1987 California Pesticide Use Report compiled by the California Department of Food and Agriculture (CDFA) were 13.65 million pounds of

TABLE B-3. COMPARISON OF CONTRIBUTIONS TO TOTAL PESTICIDE USE BY  
THE TOP PESTICIDE USING STATES

State	Percent of total pesticide use	Percent of total herbicide use	Percent of total insecticide use	Percent contribution of herbicides to total State pesticide use
Iowa	8.9	10.6	0.7	98.6
Illinois	8.4	9.9	1.0	97.9
Minnesota	5.9	6.9	0.9	97.4
Texas	5.7	5.9	4.8	85.6
California	5.3	3.0	15.7	48.3
Total	34.2	36.3	23.1	---

1,3-dichloropropene (Telone®) and 6.0 million pounds of methyl bromide. Registration of 1,3-dichloropropene was suspended in California in 1990 and the suspension has not been lifted. This fumigant is also undergoing special review by EPA Office of Pesticide Programs (OPP). The RFF data base showed that California reported use of 12 insecticides other than DBCP in the data base. The next-highest insecticide-using State is Georgia, with 11.9 million pounds of 14 AI's reported in the data base. In this case chlorothalonil, a fungicide, accounted for approximately one-third of the insecticide use. However, DBCP and ethylene dibromide, a fumigant that had all of its agricultural uses cancelled in 1990, accounted for 17.9 percent and 27.1 percent of the total insecticide use, respectively. Thus, approximately 45 percent of the insecticide use in Georgia has been replaced with other insecticides.

Pesticide use in ozone nonattainment areas of the States is also presented in Table B-1. Since the insecticide data base did not contain county-level information, the amount of insecticide used in ozone nonattainment areas was approximated. Fifteen States were designated with no ozone nonattainment areas. These include Iowa and Minnesota, two of the largest pesticide-using States in the country.

The highest herbicide use in ozone nonattainment areas was found in California (12.2 million pounds of AI's), which has 35 counties with whole or partial nonattainment status. The AI's with the highest use in California were DCPA (1.1 million pounds), molinate (0.97 million pounds), and glyphosate (0.96 million pounds). The State with the next highest herbicide use in nonattainment areas is Michigan (11.2 million pounds of AI's), which has 37 counties with whole or partial nonattainment status. The AI's with the highest use in Michigan were atrazine (2.4 million pounds), metolachlor (1.9 million pounds), alachlor (1.4 million pounds), and EPTC (1.1 million pounds). Together California and Michigan account for 50 percent of the herbicide use in ozone nonattainment areas nationwide. Connecticut, Rhode Island, Massachusetts, and New Jersey were listed as entirely

ozone nonattainment areas such that 100 percent of these States' pesticide use was in ozone nonattainment areas.

#### B.3.1 Attachments

The attachments provide a more detailed presentation of the data obtained from the two RFF data bases. Information on the individual AI's by State and county is available through the Pesticide or Pest field and FIPS field, respectively. The pesticide code and FIPS code keys are provided in Attachment 1.

#### B.3.2 Summary

Certain weaknesses of the data base should be noted. The data contained in the data base are outdated. Several widely used AI's have had their registrations cancelled by EPA since the data base was compiled. While the data base still contains important historical data in these cases, the information is not an accurate representation of current uses of these specific AI's. A significant impact may occur at the county- or State-levels, especially for States like California where once heavily used AI's have been cancelled.

#### B.4 REFERENCES FOR APPENDIX B

1. Gianessi, L.P., C. Puffer. Herbicide Use in the United States National Summary Report. Quality of the Environment Division, Resources for the Future. December 1990, Revised April 1991. 128 p.
2. Aspelin, A. L., A. H. Grube, and V. Kibler. Pesticide Industry Sales and Usage: 1989 Market Estimate. Economic Analysis Branch, Biological and Economic Analysis Division, Office of Pesticide Programs. U. S. Environmental Protection Agency. July 1991. 21 p.

# ATTACHMENT 1

## Structure for herbicide data base.

Field	Field Name	Type	Width	Decimal
1	FIPS	character	5	
2	CRO	character	3	
3	PEST	character	4	
4	ACTES	numeric	10	
5	PCT	numeric	5	1
6	RATE	numeric	6	3
7	ACTRT	numeric	9	
8	LBSAI	numeric	8	
9	OX	numeric	1	

## Structure for insecticide data base.

Field	Field Name	Type	Width	Decimal
1	AC87	numeric	9	
2	CROP	character	16	
3	PESTICIDE	character	16	
4	STATE	character	15	
5	PCTFNL	numeric	3	
6	LBSFNL	numeric	7	2
7	LBSAI	numeric	9	
8	ACTRT	numeric	9	

## KEY:

FIPS	standard 5-digit county code
STATE	State name
CRO	crop code
CROP	crop name
PEST	pesticide code
PESTICIDE	pesticide name
ACRES, AC87	harvested crop acreage of the crop in the county (from 1987 Census of Agriculture)
PCT, PCTFNL	percent of acres treated with specified active ingredient
RATE, LBSFNL	Average annual use per treated acre with specified active

	ingredient. (lbs AI/Acre/year)
ACTRT	total acres treated in county with specified active ingredient.
LBSAI	total pounds of active ingredient used on specified crop in the county (ACTRT x RATE)
OX	county ozone nonattainment status

# PESTICIDE CODES

1002	ACTIFLUORFEN	1889	MCPS
1005	DICLOFOP	1900	NAPROPAMIDE
1011	METOLACHLOR	1903	THIOBENCARB
1018	NORFLURAZON	1910	SETHOXYDIM
1051	PICLORAM	1913	CHLORSULFURON
1098	BENSULIDE	1948	ENDOTHALL
1099	GLYPHOSATE	1950	DIQUAT
1109	TERBACIL	1963	TEBUTHIURON
1116	BROMOXYNIL	1974	DIPROPETRYN
1124	MSMA	1975	METRIBUZIN
1176	BARBAN	1977	TERBUTRYN
1183	CHLORPROPHAM	1979	PROPACINE
1191	PROPACHLOR	1980	ATRAZINE
1282	PROPANIL	1981	SIMAZINE
1287	BENTAZON	1982	AMETRYN
1289	DALAPON	1984	SIDURON
1298	DICAMBA	1987	PROMETRYN
1299	CHLORAMBEN	1988	TRICLOPYR
1302	2,4-D	1991	DIURON
1305	MCPA	1993	LINURON
1307	NAPTALAM	1998	FLUOMETURON
1308	2,4-DB	2053	CHLOROXURON
1309	BIFENOX	2069	CYCLOATE
1361	TRIFLURALIN	2070	HEXAZINONE
1362	BENEFIN	2158	PROPHAM
1366	DIPHENAMID	2220	PHENMEDIPHAM
1369	CYANAZINE	2250	PYRAZON
1374	DIFENZOQUAT	4000	OXYFLUORFEN
1375	DINOSES	4001	DSMA
1396	PROFLURALIN	4002	CLOPYRALID
1397	FLUCHLORALIN	4003	METSULFURON
1414	EPTC	4004	THIAMETURON
1417	MOLINATE	4005	IMAZIQUIN
1419	PEBULATE	4007	TRIDIPHANE
1422	VERNOLATE	4008	CHLORIMURON
1477	MCPP	4009	LACTOFEN
1616	PARAQUAT	4010	FOMESAFEN
1629	PENDIMETHALIN	5000	CLOMAZONE
1790	TRIALATE	5003	FENOXAPROP
1809	BROMACIL	9000	IMAZETHAPYR
1829	BUTYLATE	9007	FLUAZIFOP
1863	ALACHLOR	9009	ETHALFLURALIN
1863	DICHLOROBENIL	9012	ETHOFUMESATE
1867	ISOPROPALIN	9014	DESMEDIPHAM
1872	DCPA	9015	DIETHYL-ETHYL
1873	ORYZALIN	9016	DIALATE
1885	CDAA	9048	ASULAM
1888	PRONAMIDE	9096	METHAZOLE

# CROP CODE CONCORDANCE

## CRO CROP

100	BRUSSEL SPROUTS	654	OTHER HAY
101	SWEET PEPPERS	670	TOBACCO
102	ARTICHOKES	690	PEANUTS
103	STRAWBERRIES	700	CITRUS
104	GREEN PEAS	701	APPLES
105	PECANS	702	PEACHES
107	SUGARBEETS	703	PEARS
108	ALMONDS	704	CHERRIES
109	BROCCOLI	705	WATERMELONS
110	CAULIFLOWER	706	TOMATOES
111	GRAPES	707	SWEET CORN
112	NECTARINES	709	ONIONS
115	WALNUTS	710	LETTUCE
116	ASPARAGUS	711	GREEN BEANS
117	GARLIC	712	CUCUMBERS
118	COLLARDS	713	CELERY
119	MELONS	714	CARROTS
120	PLUMS	715	CANTALOUPE
121	SUNFLOWERS	716	CABBAGE
122	APRICOTS	717	POTATOES
123	AVOCADOS	800	DRY BEANS
126	SPINACH	801	DRY PEAS
127	SQUASH	842	PASTURE
128	BEETS	910	MINT
135	OLIVES	911	HOPS
136	PISTACHIOS	913	FILBERTS
139	RYE	914	CRANBERRIES
140	SAFFLOWER	915	BLACKBERRIES
143	PUMPKINS	941	HOT PEPPERS
145	FIGS	943	FLAX
147	RADISHES	949	SCD
150	EGGPLANT	952	SUGARCANE
152	OKRA	999	GUAR
153	SWEET POTATOES		
160	DATES		
236	RASPBERRIES		
243	KIWI		
244	POMEGRANATES		
245	GREEN ONIONS		
400	BLUEBERRIES		
401	SEED CROPS		
502	PARSLEY		
520	COTTON		
530	CORN		
533	CATS		
535	BARLEY		
540	WHEAT		
570	SORGHUM		
600	SOYBEANS		
605	RICE		
653	ALFALFA		



State	Two Digit FIPS code
Alabama	01
Arizona	04
Alaska	02
Arkansas	05
California	06
Colorado	08
Connecticut	09
Delaware	10
Florida	12
Georgia	13
Hawaii	15
Idaho	16
Illinois	17
Indiana	18
Iowa	19
Kansas	20
Kentucky	21
Louisiana	22
Maine	23
Maryland	24
Massachusetts	25
Michigan	26
Minnesota	27
Mississippi	28
Missouri	29
Montana	30
Nebraska	31
Nevada	32
New Hampshire	33
New Jersey	34
New Mexico	35
New York	36
North Carolina	37
North Dakota	38
Ohio	39
Oklahoma	40
Oregon	41
Pennsylvania	42
Rhode Island	44
South Carolina	45
South Dakota	46
Tennessee	47
Texas	48
Utah	49
Vermont	50
Virginia	51
Washington	53
West Virginia	54
Wisconsin	55
Wyoming	56



ATTACHMENT 2

Record#	PESTICIDE	LBSAI
1	DBCP	29072029
2	EDB	12409524
3	CHLOROTHALONIL	8875999
4	CARBARYL	8620584
5	METHYL PARATHION	7650238
6	CARBOFURAN	7154396
7	DINOSEB	6846644
8	ALDICARB	5317156
9	ETHOPROP	2486933
10	METHOMYL	2345308
11	DISULFOTON	2021997
12	DIAZINON	1842044
13	LINDANE	561045
14	OXAMYL	410083
15	FENAMIPHOS	406622
16	2,4-5T	386698



ATTACHMENT 3

Attachment 3 contains data on individual herbicide use for ozone nonattainment counties nationwide. Due to its length this attachment has not been provided here but is available on request.



TABLE 1. HERBICIDE USAGE RANKED NATIONWIDE

Active Ingredient	Pounds Used
Atrazine	68232131
Alachlor	55025302
Metolachlor	49544375
EPTC	37119783
2,4-D	33074201
Trifluralin	27005509
Cyanazine	22847387
Butylate	19070536
Pendimethalin	12475522
Glyphosate	11535166
Dicamba	11254300
Bentazon	8190359
Propanil	7487432
MSMA	4968375
Metribuzin	4792132
Molinate	4396189
MCPA	4332397
Propachlor	4313802
Propazine	3972392
Simazine	3903902
Ethalfuralin	3506483
Triallate	3505008
Chloramben	2989035
Picloram	2933901
Paraquat	2825000
Clomazone	2713716
Bromoxynil	2620914
Linuron	2599149
Fluometuron	2391268
DCPA	2008871
Diuron	1966524
Prometryn	1793996
Norflurazon	1740280
DSMA	1655019
Diclofop	1449949

Active Ingredient	Pounds Used
Oryzalin	1413826
Acifluorfen	1404719
2,4-DB	1352037
Thiobencarb	1351709
Bromacil	1146606
Benefin	1146339
Cycloate	1120883
Terbutryn	1106989
Imaziquin	1072648
Asulam	1057773
Diphenamid	910984
Vernolate	848840
Sethoxydim	838065
Fluazifop	726637
Napropamide	679147
Pebulate	649317
Naptalam	637468
Profluralin	618729
Tebuthiuron	606009
Oxyfluorfen	583158
Bensulide	541686
Diethyl-Ethyl	492562
Dipropetryn	491456
Dalapon	445549
Dinoseb	398862
Terbacil	376118
Hexazinone	343166
Imazethapyr	332646
Ethofumesate	320393
Propham	309650
Pyrazon	305777
Methazole	297520
Chlorimuron	288897
Difenzoquat	281812
Chlorpropham	247956
Pronamide	247499
Fomesafen	226347
Tridiphane	222444



Active Ingredient	Pounds Used
Endothall	196078
Ametryn	183338
Phenmedipham	166142
Diquat	160713
Desmedipham	134524
Bifenox	125147
Diallate	119250
Lactofen	101841
Isopropalin	97659
Chlorsulfuron	76966
Triclopyr	70964
Chloroxuron	58642
Dichlobenil	58066
Thiameturon	54839
Barban	51535
MCPB	42445
Metsulfuron	40881
Clopyralid	26208
Fenoxaprop	26154
CDAA	22012
Fluchloralin	20095
MCPP	17950
Siduron	3559



ATTACHMENT 5

TABLE 1. HERBICIDE USAGE FOR OZONE NONATTAINMENT AREAS

Pest Code	Pounds Used
-----	-----
1002	109726
1005	68506
1011	7398163
1018	201668
1051	40159
1098	153715
1099	2223640
1109	152457
1116	216040
1124	53384
1176	14474
1183	91665
1191	46431
1282	626907
1287	692275
1289	211435
1298	709061
1299	766220
1302	1952924
1305	441538
1307	100282
1308	212581
1309	10637
1361	1665625
1362	115303
1366	363813
1369	2688130
1374	33954
1375	56967
1396	47595
1397	17736
1414	2896725
1417	1289449
1419	296238
1432	103195
1477	12076
1616	992326
1629	1439202
1790	11688
1809	123681
1839	2333538
1863	5967411
1865	16839
1867	6603
1872	1289430
1873	842561
1885	11711
1888	83948
1889	5005
1900	450935
1903	432190

TABLE 1. HERBICIDE USAGE FOR OZONE NONATTAINMENT AREAS CONT

Pest Code	Pounds Used
1910	75777
1913	1592
1948	94494
1950	40608
1963	1890
1974	7117
1975	723406
1977	18824
1979	119335
1980	9630754
1981	1221504
1982	64735
1984	3559
1987	335275
1988	9060
1991	542325
1993	750603
1998	18310
2053	47678
2069	227766
2070	119927
2158	66718
2220	53537
2250	246520
4000	462086
4001	16488
4002	1247
4003	707
4004	2716
4005	89290
4007	4901
4008	37366
4009	3620
4010	12976
5000	244123
5003	1499
9000	23798
9007	63434
9009	134840
9012	112289
9014	41128
9015	255509
9048	893030
9096	851

**APPENDIX C**  
**LABORATORY TEST PROCEDURES FOR**  
**VOC CONTENT IN PESTICIDES**



## METHOD DEVELOPMENT SUMMARY:

### DIRECT MEASUREMENT OF VOLATILE ORGANICS IN LIQUID PESTICIDE FORMULATIONS

#### 1. METHODS EVALUATED

Two methods for measuring the volatile organic (VO) content of liquid pesticides were evaluated. The first method, widely used in the industry, involves measurement of volatile content by thermogravimetric analysis (TGA), measurement of water content by Karl Fischer titration, and calculation of VO content as the difference. The proposed method, Volatile Organics in Pesticides (VOP) Method, is a purge and trap procedure at constant temperature. The VOP Method allows direct gravimetric measurement of nonvolatiles, VO, and water in a single analysis. Both methods should be conducted in triplicate and the average reported.

##### 1.1 Thermogravimetric Analysis

The determination of volatile material in pesticide formulations is typically determined by thermogravimetric analysis (TGA). The "American Standard Test Method (ASTM) for Compositional Analysis by Thermogravimetry" is included for reference.<sup>6</sup> The procedures in section 11 of the referenced method should be followed to determine the volatile material in samples of the pesticide with the following additional specifications:

11.9: Purge samples with nitrogen at 54°C and with a constant flow rate between 50 to 100 ml/min. (A temperature of 54°C is used to test the chemical stability of agricultural formulations during development. Little or no decomposition of any type is considered to occur at that temperature.)

11.10: Purge until a constant weight is achieved or for a maximum of 4 hours, whichever comes first.

12.1.1: This basic equation should be applied to determine the weight percent of volatiles in the sample. (The weight

lost is divided by the original weight and multiplied by 100 to determine the percent volatile material.)

Water content of a pesticide may be determined by Karl Fischer titration. Volatile organic (VO) content can then be determined as the difference between volatile content and water content.

The method is less precise for water-based formulations than it is for solvent-based formulations, and the imprecision increases as water content increases.

The California Department of Pesticide Regulation (DPR) is currently developing a TGA method to determine the VOC content of various pesticide formulations. The major differences between the California method and this method are the temperature and duration of the test. In the California method, the sample is heated at a temperature of 115°C until a constant weight is attained for a specified period of time, usually about 15 minutes. The overall time required for the test is approximately one hour. If the active ingredient is known to be unstable or volatilize at the test temperature, a lower heating temperature and longer heating time are to be used. The DPR has stated that lower heating temperatures have been required for some of the formulations tested to date. Further information concerning the California test method can be obtained from Ms. Judy Pino, Environmental Monitoring Section, California EPA/DPR; phone number (916) 654-1141.

### 1.2 VOP Method

Recently, a method that allows the direct measurement of volatile organic compound (VOC) content of water-based coatings was adapted to pesticide analysis. The method is a purge and trap procedure conducted at constant temperature, similar to EPA Method 24. The procedure involves purging volatiles from a weighed sample of material with dry nitrogen at an appropriate temperature (54°C for pesticide formulations), adsorption of VO in the volatile fraction onto activated charcoal in pre-weighed tubes, determination of final weights for both the sample residue



and the charcoal tubes, and computation of weight percent of VO in the original sample.

Water, if present, can also be measured directly by adding collection tubes containing an anhydrous material (e.g., Drierite) to the exit port of the last charcoal tube. Water, which is not adsorbed by charcoal, is collected quantitatively in the Drierite tubes. The weight gain of the Drierite tubes represents the weight of water present in the original sample. The weight percent of water in the liquid pesticide is then calculated.

Nonvolatiles are measured directly by determining the weight of the residue after heating. Weight percent nonvolatiles is then calculated in the usual way.

Mass balance can be demonstrated by computing the sum of weight percent VO, weight percent water, and weight percent nonvolatiles. The sum is typically in the range of 96 to 99 percent. If the sum is less than 95 percent, the results should be discarded. The material loss is generally attributed to a leak that develops during the 4-hour heating period.

The method removes some of the inherent imprecision in the TGA/Karl Fischer method and could be easily extended to include speciation of VO. This could be accomplished by desorption (liquid or thermal) of the charcoal (or other suitable sorbent) and analysis by gas chromatography with mass selective detection (GC-MS). Individual VO could be identified by library matching of mass spectral data and quantified by the use of appropriate standards.

Additional work is being conducted to develop precision and bias data for this method. Information on the status of this work can be obtained by contacting the EPA Work Assignment Manager, Dr. Joseph E. Kroll, in Research Triangle Park, North Carolina. Dr. Kroll can be reached at (919) 541-2952.

## **2.0 COMPARISON OF TGA AND VOP METHOD**

In the current study, weight percent nonvolatiles measured by thermogravimetric analysis (TGA) and by Volatile Organics in Pesticides Method (VOP) were compared to see if there was any

relative bias in the two methods. Twelve commercial pesticides, sold as emulsifiable concentrates, were used in the study. Of the twelve, ten were solvent-based and two were water-based. All ten of the solvent-based and one of the water-based pesticides were analyzed by TGA. All 12 pesticides were analyzed by VOP.

A summary to TGA data for the eleven pesticides analyzed is presented in Table 1. All TGA data was collected at 54°C and the sample size was approximately 25 mg. All TGA analyses except the one with Lasso were allowed to run for 4 hours (240 min). All volatiles had been removed from Lasso within the first 90 min. Weight percent nonvolatiles ranged from 28.65 percent to 88.28 percent. The one water-based pesticide (Blazer) is indistinguishable from the solvent-based pesticides.

Hourly measurement for the samples analyzed by VOP were obtained by stopping the run, disassembling the apparatus, allowing the sealed components to cool to room temperature, weighing the appropriate components, reassembling the apparatus, and continuing the run. Using this approach, ten pesticides were allowed to run for a total heating time of 6 hours, one (Basagran) for 4 hours, and one (Lasso) for 2 hours. A summary of weight percent nonvolatiles measured by VOP, paired with appropriate TGA data, is presented in Table 2.

A statistical analysis of the paired VOP and TGA data for nonvolatiles at the end of 4 hours (2 hours for Lasso) confirmed that the two methods give equivalent results for nonvolatiles at the 95 percent confidence level. A summary of the statistical comparison is presented in Table 3.

A summary of the VOP analysis of two water-based pesticides is given in Table 4. According to the Material Safety Data Sheet (MSDS) for Blazer, the formulation contains 8.5 percent butyl cellosolve, which has a boiling point of 171°C. Because of its high boiling point, only 3.78 percent of the butyl cellosolve was collected on the charcoal tubes after 6 hours at 54°C. The MSDS for Basagran claims no VO is present and none (-0.21 percent) was measured by VOP after 3 hours at 54°C.

### 3. CONCLUSIONS

The two methods, TGA and VOP, give equivalent results for nonvolatiles. VOP offers the added advantage of also directly measuring VO and water in the same analysis. Neither of the two methods differentiates between volatile organics from solvent, from emulsifiers, or from active ingredients. VOP has the potential for speciation, which would allow subtraction of volatilized active ingredients, and/or other exempt compounds, from the total VO. In addition, if a liquid pesticide contains no water, EPA Method 24 may be used.



TABLE 1. WEIGHT PERCENT NONVOLATILES IN LIQUID PESTICIDES BY TGA

Weight Percent Nonvolatiles at 10-min Intervals by Thermogravimetric Analysis

Time (min)	Acclaim	Baythroid	Blazer <sup>a</sup>	Buctril	Folex 6 EC	Carlon 4	Lasso	Poast	Poast Plus	Prowl 4E	Treflan 4 EC	Weedone LV6
0	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
10	54.95%	86.26%	47.84%	50.37%	80.30%	91.81%	60.60%	73.77%	90.31%	63.98%	86.44%	95.50%
20	50.95%	83.17%	44.43%	44.60%	77.33%	86.80%	56.15%	54.44%	88.94%	60.15%	82.74%	93.06%
30	49.94%	81.27%	42.95%	43.57%	76.43%	83.28%	54.86%	41.49%	88.46%	59.44%	79.96%	91.53%
40	49.59%	80.16%	42.25%	43.31%	76.04%	80.66%	54.43%	34.72%	88.31%	59.23%	77.90%	90.58%
50	49.41%	79.44%	41.78%	43.22%	75.81%	78.63%	54.23%	31.74%	88.24%	59.15%	76.14%	89.97%
60	49.46%	78.94%	41.43%	43.16%	75.71%	77.03%	54.10%	30.39%	88.20%	59.11%	74.62%	89.57%
70	49.39%	78.56%	41.19%	43.13%	75.63%	75.77%	54.01%	29.72%	88.17%	59.11%	73.42%	89.28%
80	49.38%	78.28%	40.98%	43.11%	75.53%	74.75%	53.95%	29.34%	88.15%	59.09%	72.04%	89.05%
90	49.33%	78.06%	40.80%	43.09%	75.51%	73.99%	53.90%	29.13%	88.13%	59.07%	70.77%	88.92%
100	49.32%	77.90%	40.66%	43.07%	75.45%	73.30%	53.85%	28.98%	88.11%	59.05%	69.62%	88.79%
110	49.32%	77.76%	40.52%	43.06%	75.41%	72.73%	53.82%	28.88%	88.10%	59.04%	68.57%	88.69%
120	49.32%	77.64%	40.49%	43.04%	75.37%	72.25%	53.78%	28.78%	88.08%	59.03%	67.64%	88.62%
130	49.32%	77.54%	40.42%	43.03%	75.36%	71.84%		28.77%	88.06%	59.02%	66.77%	88.56%
140	49.32%	77.43%	40.35%	43.02%	75.32%	71.48%		28.75%	88.05%	59.02%	65.98%	88.50%
150	49.31%	77.36%	40.26%	43.00%	75.33%	71.17%		28.71%	88.03%	59.01%	65.25%	88.46%
160	49.29%	77.28%	40.20%	42.99%	75.33%	70.89%		28.70%	88.01%	59.02%	64.56%	88.43%
170	49.27%	77.23%	40.14%	42.98%	75.30%	70.65%		28.68%	87.95%	59.01%	63.91%	88.41%
180	49.26%	77.18%	40.08%	42.97%	75.30%	70.42%		28.67%	87.90%	59.01%	63.31%	88.37%
190	49.27%	77.15%	40.03%	42.96%	75.26%	70.22%		28.67%	87.86%	59.01%	62.73%	88.35%
200	49.25%	77.11%	39.99%	42.95%	75.26%	70.03%		28.66%	87.84%	58.99%	62.19%	88.33%
210	49.26%	77.07%	39.94%	42.95%	75.26%	69.85%		28.66%	87.82%	58.98%	61.64%	88.31%
220	49.25%	77.04%	39.90%	42.94%	75.25%	69.69%		28.65%	87.80%	58.98%	61.13%	88.30%
230	49.26%	77.01%	39.87%	42.94%	75.24%	69.52%		28.65%	87.78%	58.98%	60.62%	88.29%
240	49.25%	76.99%	39.83%	42.94%	75.24%	69.36%		28.64%	87.77%	58.98%	60.16%	88.28%

<sup>a</sup>Water-based pesticide. All others are solvent-based.

TABLE 2. COMPARISON OF RESULTS WITH MODIFIED METHOD 24 AND TGA

Pesticide	Method	Weight Percent Nonvolatiles at 60-min Intervals <sup>a</sup>								
		0 min	60 min	120 min	180 min	240 min	300 min	360 min		
Acclaim 1EC	MM24 TGA	100.00% 100.00%	48.03% 49.46%	46.49% 49.32%	46.37% 49.26%	46.35% 49.25%	46.31%	46.27%		
Basagran <sup>b</sup>	MM24 TGA	100.00% --	52.85% --	51.57% --	50.92% --	--	--	--		
Baythroid 2	MM24 TGA	100.00% 100.00%	81.28% 78.94%	78.49% 77.64%	76.97% 77.18%	76.56% 76.99%	76.34%	76.16%		
Blazer <sup>b</sup>	MM24 TGA	100.00% 100.00%	41.50% 41.43%	39.82% 40.49%	39.21% 40.08%	38.80% 39.83%	38.62%	38.46%		
Buctril	MM24 TGA	100.00% 100.00%	42.64% 43.16%	42.22% 43.04%	42.06% 42.97%	42.11% 42.94%	41.99%	41.94%		
Folex 6 EC	MM24 TGA	100.00% 100.00%	75.53% 75.71%	74.82% 75.37%	74.59% 75.30%	74.53% 75.24%	74.29%	74.27%		
Garlon 4	MM24 TGA	100.00% 100.00%	83.49% 77.03%	77.56% 72.25%	73.82% 70.42%	71.27% 69.36%	70.08%	69.18%		
Lasso	MM24 TGA	100.00% 100.00% 100.00%	53.16% 53.20% 53.35%	51.59% 52.83% 53.01%	51.33%	51.08%	--	--		
Poast	MM24 TGA	100.00% 100.00%	47.39% 30.39%	31.42% 28.77%	28.51% 28.67%	28.03% 28.64%	27.78%	27.48%		
Poast Plus	MM24 TGA	100.00% 100.00%	87.75% 88.20%	87.30% 88.08%	87.20% 87.90%	87.13% 87.77%	87.00%	86.92%		
Prowl 4E	MM24 TGA	100.00% 100.00%	58.33% 59.11%	57.06% 59.03%	56.94% 59.01%	56.90% 58.98%	--	--		
Treflan E.C.	MM24 TGA	100.00% 100.00%	76.88% 74.62%	72.04% 67.64%	68.11% 63.31%	64.34% 60.16%	62.79%	61.05%		
Weedone LV6	MM24 TGA	100.00% 100.00%	92.67% 89.57%	90.05% 88.62%	89.09% 88.37%	88.57% 88.28%	88.25%	88.11%		

<sup>a</sup>All runs conducted at 54 °C.

<sup>b</sup>Water-based pesticide

TABLE 3. STATISTICAL COMPARISON OF MODIFIED METHOD 24 AND TGA

Pesticide	Nonvolatiles (Wt. %) <sup>a</sup>		Paired-Data Statistical Analysis		
	Modified Method 24	TGA	Difference $X_i$	$(X_i - \bar{X})$	$(X_i - \bar{X})^2$
Acclaim 1EC	46.35%	49.25%	-2.90	-2.62	6.84
Baythroid 2	76.56%	76.99%	-0.43	-0.15	0.02
Blazer <sup>b</sup>	38.80%	39.83%	-1.03	-0.68	0.47
Buctril	42.11%	42.94%	-0.83	-0.54	0.30
Folex 6 EC	74.53%	75.24%	-0.71	-0.42	0.18
Garlon 4	71.27%	69.36%	1.90	2.19	4.80
Lasso	51.59% <sup>c</sup>	52.92% <sup>d</sup>	-1.33	-1.04	1.08
Poast	28.03%	28.64%	-0.61	-0.33	0.11
Poast Plus	87.13%	87.77%	-0.64	-0.36	0.13
Prowl 4E	56.90%	58.98%	-2.08	-1.79	3.20
Treflan E.C.	64.34%	60.16%	4.18	4.47	19.97
Weedone LV6	88.57%	88.28%	0.29	0.58	0.34

$$\Sigma X_i = -4.18$$

$$\Sigma (X_i - \bar{X})^2 = 37.46$$

$$n = 12$$

$$\bar{X} = -0.348$$

$$s_{\bar{X}} = \sqrt{\frac{\Sigma (X_i - \bar{X})^2}{(n-1)n}} = 0.5327$$

Student's *t* test:

$$df = n-1 = 11$$

confidence level = 95%

$$t_{\text{table}} = \pm 2.201$$

$$t_{\text{calc}} = \frac{\bar{X}}{s_{\bar{X}}} = -0.653$$

∴ The two methods give equivalent results for nonvolatiles at the 95% confidence level.

<sup>a</sup>Volatiles were purged at 54°C for 240 min for all pesticides except Lasso.

<sup>b</sup>Blazer is water-based; all others in list are solvent-based.

<sup>c</sup>All volatiles had been removed from Lasso in 120 min.

<sup>d</sup>Average of two 120-min TGA runs.

**TABLE 4.**  
**ANALYSIS OF WATER-BASED PESTICIDES**  
**BY MODIFIED METHOD 24<sup>a</sup>**

Water-Based Pesticide	Time (min)	Weight % Nonvol.	Weight % VOC	Weight % Water	Mass Balance Total
Blazer	60	41.50%	5.13%	50.37%	97.00%
	120	39.82%	3.83%	53.06%	96.71%
	180	39.21%	3.40%	54.05%	96.66%
	240	38.80%	3.37%	54.33%	96.50%
	300	38.62%	3.56%	53.55%	95.72%
	360	38.46%	3.78%	54.34%	96.58%
Basagran	60	52.85%	1.19%	40.73%	94.78%
	120	51.57%	-0.09%	43.82%	95.30%
	180	50.92%	-0.21%	45.32%	96.03%

<sup>a</sup>All analyses were conducted at 54°C.





## Standard Test Method for Compositional Analysis by Thermogravimetry<sup>1</sup>

This standard is issued under the fixed designation E 1131; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method is intended to provide a general technique incorporating thermogravimetry to determine the amount of highly volatile matter, medium volatile matter, combustible material, and ash content of compounds. This test method will be useful in performing a compositional analysis in cases where agreed upon by interested parties.

1.2 This test method is applicable to solids and liquids.

1.3 The temperature range of test is typically room temperature to 1000°C. Composition between 1 and 100 weight % of individual components may be determined.

1.4 This test method utilizes an inert and reactive gas environment.

1.5 Computer or electronic-based instruments, techniques, or data treatment equivalent to this method may also be used. Users of this test method are expressly advised that all such instruments or techniques may not be equivalent. It is the responsibility of the user of this test method to determine the necessary equivalency prior to use. In the case of dispute, only the manual procedures described in this test method are to be considered valid.

1.6 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 1603 Test Method for Carbon Black in Olefin Plastics<sup>2</sup>

D 3172 Practice for Proximate Analysis of Coal and Coke<sup>3</sup>

E 472 Practice for Reporting Thermoanalytical Data<sup>4</sup>

E 473 Definitions of Terms Relating to Thermal Analysis<sup>4</sup>

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>4</sup>

E 914 Practice for Evaluating Temperature Scale for Thermogravimetry<sup>4</sup>

### 3. Terminology

#### 3.1 Definitions:

3.1.1 The definitions relating to thermal analysis appearing in Definitions E 473 shall be considered applicable to this test method.

3.1.2 *thermogravimetry*—technique in which the mass of a substance is measured as a function of temperature or time, while the substance is subjected to a controlled temperature program.

#### 3.2 Descriptions of Terms Specific to This Standard:

3.2.1 *highly volatile matter*—moisture, plasticizer, residual solvent or other low boiling (200°C or less) components.

3.2.2 *medium volatile matter*—medium volatility materials such as oil and polymer degradation products. In general, these materials degrade in the temperature range 200 to 750°C.

3.2.3 *combustible material*—oxidizable material not volatile (in the unoxidized form) at 750°C, or some stipulated temperature dependent on material. Carbon is an example of such a material.

3.2.4 *ash*—nonvolatile residues in an oxidizing atmosphere which may include metal components, filler content or inert reinforcing materials.

3.2.5 *mass loss plateau*—a region of a thermogravimetric curve with a relatively constant mass.

### 4. Summary of Method

4.1 This test method is an empirical technique using thermogravimetry in which the mass of a substance, heated at a controlled rate in an appropriate environment, is recorded as a function of time or temperature. Mass loss over specific temperature ranges and in a specific atmosphere provide a compositional analysis of that substance.

### 5. Significance and Use

5.1 This test method is intended for use in quality control, material screening, and related problem solving where a compositional analysis is desired or a comparison can be made with a known material of the same type.

5.2 The parameters described should be considered as guidelines. They may be altered to suit a particular analysis, provided the changes are noted in the report.

5.3 The proportion of the determined components in a given mixture or blend may indicate specific quality or end use performance characteristics. Particular examples include the following:

5.3.1 Increasing soot (carbon) content of used diesel lubricating oils indicates decreasing effectiveness.

5.3.2 Specific carbon-to-polymer ratio ranges are required in some elastomeric and plastic parts in order to achieve desired mechanical strength and stability.

5.3.3 Some filled elastomeric and plastic products require specific inert content (for example, ash, filler, reinforcing agent, etc.) to meet performance specifications.

5.3.4 The volatile matter, fixed carbon, and ash content of coal and coke are important parameters. The "ranking" of

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee E-37 on Thermal Measurements and is the direct responsibility of Subcommittee E37.01 on Test Methods and Recommended Practices.

Current edition approved Sept. 26, 1986. Published November 1986.

<sup>2</sup> Annual Book of ASTM Standards, Vol 08.02.

<sup>3</sup> Annual Book of ASTM Standards, Vol 05.05.

<sup>4</sup> Annual Book of ASTM Standards, Vol 14.02.

TABLE 1 Compositional Analysis Interlaboratory Test Parameters

Test Parameters by Material					
Material	Sample Mass <sup>a</sup> (mg)	Purge Gas Flow (mL/min)	Precal- ysis Purge (min)		
Coal	20	50	1		
Lubricant	10	100	1		
Polyethylene	20	50	1		
Calcium Oxalate	10	50	1		
Test Parameters by Component					
Component	Start Temper- ature °C	Rate °C/min	Final Temper- ature °C	Hold (min)	Gas
Coal <sup>a</sup>					
Highly Volatile <sup>b</sup>	50	50	110 (X)	5	N2
Medium Volatile	110	100	950 (Y)	15	N2
Combustible	950	0	950	10	Air
Ash	950	0	950 (Z)	0	Air
Lubricant					
Highly Volatile	50	20	150 (X)	2	N2
Medium Volatile	150	100	650 (Y)	5	N2
Combustible	650	20	750	0	Air
Ash	750	0	750 (Z)	1	Air
Polyethylene					
Highly Volatile	Ambient	10	150 (X)	0	N2
Medium Volatile	150	10	600 (Y)	0	N2
Combustible	300	10	750	1	Air
Ash	750	10	800 (Z)	0	Air
Calcium Oxalate Monohydrate <sup>c</sup>					
Highly Volatile	Ambient	10	200 (X)	0	N2
Medium Volatile	200	10	600 (Y)	0	N2
Combustible	600	10	800	0	Air
Ash	800	10	800 (Z)	0	Air

<sup>a</sup> Smaller sample sizes may be used to avoid instrument fouling.

<sup>b</sup> Coal is determined on a dry basis therefore the highly volatile component will not be measured. The initial mass should be measured at 110°C after the 5 min hold. If direct percentage measurements are being made, reset balance to 100 % Temperature (X) = 110°C, Mass (W) = Mass (F).

<sup>c</sup> For calcium oxalate, the component's nomenclature refers to mass loss plateaus rather than the definitions of the method.

coal increases with increasing carbon content and decreasing volatile and hydrocarbon, (medium volatility) content.

## 6. Interferences

6.1 This test method depends upon distinctive thermostability ranges of the determined components as a principle of the test. For this reason, materials which have no well-defined thermostable range, or whose thermostabilities are the same as other components, may create interferences. Particular examples include the following:

6.1.1 Oil-filled elastomers have such high molecular weight oils and such low molecular weight polymer content that the oil and polymer may not be separated based upon temperature stability.

6.1.2 Ash content materials (metals) are slowly oxidized at high temperatures and in an air atmosphere, so that their mass increases (or decreases) with time. Under such conditions, a specific temperature or time region must be identified for the measurement of that component.

6.1.3 Polymers, especially neoprene and acrylonitrile butadiene rubber (NBR), carbonize to a considerable extent, giving low values for the polymer and high values for the

TABLE 2 Precision Test Values

NOTE 1—Where:  $\bar{X}$  = average component concentration in weight percent,  $I_r$  = repeatability interval as defined by Practice E 691, and  $I_R$  = reproducibility interval as defined by Practice E 691.

NOTE 2—Three materials are reported here on a dry basis, with no highly volatile component. Polyethylene is reported on a dry ash-free basis.

	$\bar{X}$	$I_r$	$I_R$
Highly Volatile Matter, %			
calcium oxalate monohydrate <sup>a</sup>	11.6	0.3	0.5
Medium Volatile Matter, %			
high volatility bituminous coal	40.4	1.8	3.3
used diesel lubricating oil	96.7	0.7	1.1
carbon filled polyethylene	97.3	0.4	0.5
calcium oxalate monohydrate	18.1	0.5	0.6
Combustible Matter, %			
high volatility bituminous coal	53.6	1.3	2.8
used diesel lubricating oil	2.5	0.4	0.5
carbon filled polyethylene	2.7	0.4	0.5
calcium oxalate monohydrate	30.8	0.6	1.1
Ash, %			
high volatility bituminous coal	6.1	1.1	2.2
used diesel lubricating oil <sup>b</sup>	0.8	0.7	1.2
calcium oxalate monohydrate	39.5	1.3	1.3

<sup>a</sup> Although the four components measured in calcium oxalate monohydrate do not strictly follow the definitions of this test method, their four well defined mass loss plateaus provide precision data indicative of a well behaved specimen.

<sup>b</sup> Although outside the scope of this test method, the ash component for lubricating oil is included to indicate the precision to be expected when measuring components below 1 %.

carbon. Approximate corrections can be made for this if the type of polymer is known.

6.1.4 Certain pigments used in rubber lose weight on heating. For example, some pigments exhibit water loss in the range 500 to 600°C, resulting in high polymer values. Others, such as calcium carbonate, release CO<sub>2</sub> upon decomposition at 825°C, that may result in high carbon values. The extent of interference is dependent upon the type and quantity of pigment present.

## 7. Apparatus

7.1 *Thermogravimetric Analyzer*—A system of related instruments that is capable of continuously weighing a sample under atmospheric control over a selected temperature range or over a selected time period at an isothermal temperature.

7.2 *Electrobalance*, sensitive to 2 µg.

7.3 *Specimen Holder*, constructed of a material that will not decompose within the anticipated temperature range and that will not react with the specimen material.

7.4 *Temperature Sensor*.

7.5 *Furnace*, of sufficient size to enclose the specimen holder and temperature sensor, controllable from 25 to at least 1000°C (higher temperature ranges may be used).

7.6 *Temperature Programmer*.

7.7 *X-Y or Strip Chart Recorder*, with sufficient sensitivity to measure a 25 µg mass change per 1 cm of chart deflection minimum. The capability to measure the first derivative of the signal may be useful in the measurement of obscure thermostability ranges.

7.8 *Gas Flow Control Device*, with the capability of switching between inert and reactive gases.

## 8. Reagents and Materials

8.1 An inert compressed gas such as argon or nitrogen and

TABLE 3 Summary of Bias

	Compositional Analysis, %	Proximate Analysis, %	Theoretical, %
Coal			
medium volatile matter	40.4	...	...
combustible material	53.6	...	...
ash	6.1	6.2	...
volatiles	...	40.4	...
fixed carbon	...	53.9	...
Calcium Oxalate Monohydrate			
highly volatile matter	11.6	...	...
medium volatile matter	18.1	...	...
combustible material	30.8	...	...
ash	39.5	...	39.2
carbon monoxide	...	...	18.9
carbon dioxide	...	...	29.7
water	...	...	12.2

a reactive compressed gas such as air or oxygen are required for this method.

#### 8.2 Purity of Purge Gases:

8.2.1 0.01 % maximum total impurity.

8.2.2 1.0 µg/g water impurity maximum.

8.2.3 1.0 µg/g hydrocarbon impurity maximum.

8.2.4 The inert purge gas must not contain more than 10 µg/g oxygen.

### 9. Test Specimens

9.1 Specimens are ordinarily measured as received. If some heat or mechanical treatment is applied to the specimen prior to test, this treatment shall be noted in the report.

9.2 Since the applicable samples may be mixtures or blends, take care to ensure that the analyzed specimen is representative of the sample from which it is taken. If the sample is a liquid, mixing prior to taking the specimen is sufficient to ensure this consideration. If the sample is a solid, take several specimens from different areas of the sample and either combine for a single determination, or each run separately with the final analysis representing an average of the determinations. Note the number of determinations in the report.

### 10. Calibration

10.1 Calibrate the apparatus according to prescribed procedures or appropriate operating manual at the heat and purge gas flow rates to be used.

### 11. Procedure

11.1 Establish the inert (nitrogen) and reactive (air or oxygen) gases at the desired flow rates. For most analyses, this rate will be in the range of 10 to 100 mL/min. Higher

flow rates may be used for some analyses, particularly when utilizing high heating rates.

11.2 Switch the purge gas to the inert (nitrogen) gas.

11.3 Zero the recorder and tare the balance. It is recommended that this be done in a range at least one recorder setting more sensitive than that to be used in the final ash weighing.

11.4 Open the apparatus to expose the specimen holder.

11.5 Prepare the specimen as outlined in 8.2 and carefully place it in the specimen holder. Typically, a sample mass of 10 to 30 mg shall be used (see Table 4).

NOTE 1—Specimens smaller than 10 mg may be used if larger specimens cause instrument fouling or poor reproducibility.

11.6 Position the specimen temperature sensor to the same location used in calibration (See Section 10).

11.7 Enclose the specimen holder.

11.8 Record the initial mass. If the apparatus in use has provisions for direct percentage measurements, adjust to read 100 %.

11.9 Initiate the heating program within the desired temperature range. See Table 4 for suggested heating rates and temperature ranges. Record the specimen mass change continuously over the temperature interval.

11.9.1 The mass loss profile may be expressed in either milligrams or mass percent of original specimen mass. Expanded scale operation may be useful over selected temperature ranges.

11.9.2 If only one or two components of the compositional analysis are desired, specific, more limited temperature ranges may be used. Similarly, several heating rates may be used during analysis in those regions of greater or lesser interest. Isothermal periods may be necessary for some materials. See Table 4 for suggested parameters.

11.10 Once a mass loss plateau is established in the range 600 to 950°C, depending on the material, switch from inert to reactive environment.

11.10.1 If a distinct plateau is not observed in this range, the atmosphere change is made based on the zero slope indication of the recorded first derivative or upon some agreed upon temperature. Suggested temperatures for this region are given in Table 4.

11.10.2 The resolution of this region may be enhanced, where carbon is present in large quantities or of special interest, by maintaining the specimen at constant temperature for several minutes after switching environments.

11.11 The analysis is complete upon the establishment of a mass loss plateau following the introduction of the reactive gas.

11.12 Switch to the inert purge gas.

TABLE 4 Suggested Compositional Analysis Parameters

Material	Sample Size mg	Flow Rate mL/min <sup>a</sup>	Purge Time Min	Temperature				Heating Rate °C/min	Gas Switchover °C
				Initial	X	Y	Z <sup>b</sup>		
coal	20	50	5	ambient	110	900	900	10 to 150	900
elastomers	20	50	2	ambient	325	550	750	10	600
thermoplastics	20	50	2	ambient	200	600	750	10	600
lubricants	20	40 to 500	1	50	150	600	750	10 to 100	600
thermosets	20	50	2	ambient	200	550	750	10	600

<sup>a</sup> May differ depending upon instrument design.

<sup>b</sup> Z is not necessarily the final temperature.

Sample: Rubber, Lot 63

Date: 30 Sept. 83

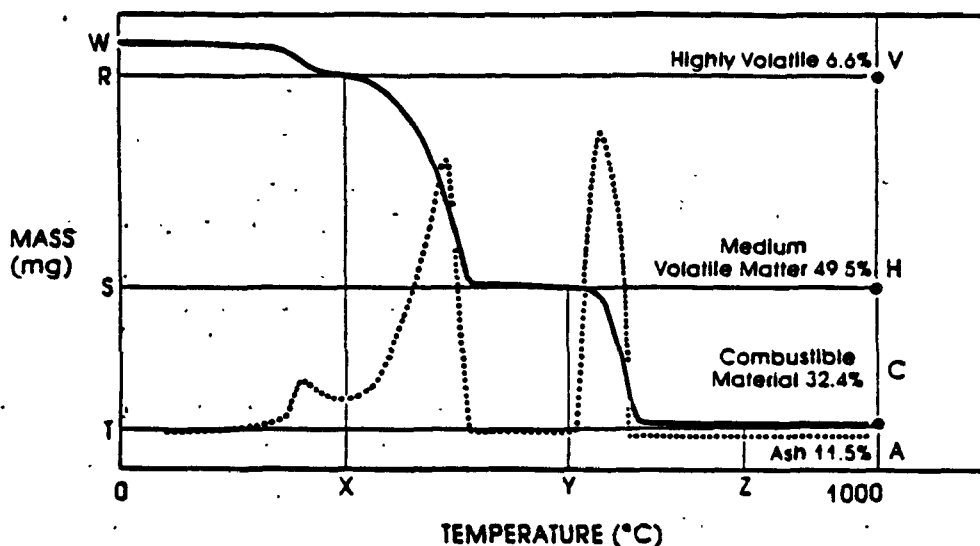


FIG. 1 Sample Thermogravimetric Curve

## 11.13 Calculate and report the sample composition.

## 12. Calculation

12.1 Highly volatile matter is represented by a mass loss measured between the starting temperature and Temperature *X* (see Fig. 1). Temperature *X* should be taken in the center of the first mass loss plateau or, if no resolvable plateau exists, at an agreed upon temperature value. Suggested values for Temperature *X* are given in Table 1.

12.1.1 Highly volatile matter content may be determined by the following equation:

$$V = \frac{W - R}{W} \times 100 \%$$

where:

*V* = highly volatile matter content, as received basis (%),  
*W* = original specimen mass (mg), and  
*R* = mass measured at Temperature *X* (mg).

12.2 Medium volatile matter is represented by the mass loss measured from Temperature *X* to Temperature *Y* (see Fig. 1). Temperature *Y* should correspond to the mass loss

plateau used for switching atmospheres.

12.2.1 Medium volatile matter content can be determined using the following equation:

$$O = \frac{R - S}{W} \times 100 \%$$

where:

*O* = medium volatile matter content, as-received basis, %,  
*R* = mass measured at Temperature *X*, (mg),  
*S* = mass measured at Temperature *Y*, (mg), and  
*W* = original specimen mass, (mg).

12.3 Combustible material content is represented by the mass loss measured from Temperature *Y* to Temperature *Z* (see Fig. 1). This region corresponds to the mass loss as a result of the oxidation of carbon to carbon dioxide.

12.3.1 Combustible material content may be calculated by the following equation:

$$C = \frac{S - T}{W} \times 100 \%$$

where:

*C* = combustible material content, as-received basis, (%),  
*S* = mass measured at Temperature *Y*, (mg),  
*T* = mass measured at Temperature *Z*, (mg) and  
*W* = original specimen mass, (mg).

12.4 The residual weight remaining after the evolution of carbon dioxide is taken as ash content. This component is measured at Temperature *Z*. This temperature is not necessarily the final temperature. Suggested values for Temperature *Z* are given in Table 4.

12.4.1 The ash components of some materials may slowly oxidize and subsequently gain or lose weight at high temperatures. In such materials, a value for Temperature *Z* must be chosen prior to such transitions.

12.4.2 The ash content may be calculated using the following equation:

Sample:	Rubber, lot 63, approximately 30 % carbon fill	
Pretreatment:	None	
Apparatus:	TG (Model XX)	
Temperature Range:	Ambient to 1000°C at 10°C/min	
Purge Gas:	Ambient to 600°C—Nitrogen 99.99 % 600°C to 1000°C—Air, Zero Grade Flow—50 mL/min	
Preliminary Purge Time:	10 min	
Determinations:	Duplicate	
Composition in Weight Percent	Highly Volatile	6.6 %
	Medium Volatile	49.5 %
	Combustible	32.4 %
	Ash	11.5 %

FIG. 2 Example Report

$$A = \frac{T}{W} \times 100 \%$$

where:

$A$  = ash content, as received basis, (%),  
 $T$  = mass measured at Temperature  $Z$ , (mg) and  
 $W$  = original specimen mass.

NOTE 2—The use of the recorded first derivative may be useful in locating the value of  $X$ ,  $Y$ , and  $Z$  by examining areas of the curve where the derivative returns to, or approaches the baseline (see Fig. 1).

### 13. Report

13.1 The report shall include the following:

13.1.1 Description of the material, including the name of the manufacturer and information on lot number and proposed chemical composition, when known,

13.1.2 Description of any sample pretreatment prior to analysis,

13.1.3 Description of the thermogravimetric analysis apparatus, including, where appropriate, the make and model of commercial equipment used,

13.1.4 Temperature range over which the various components are measured and the respective heating rates,

13.1.5 Purge gas, flow rate, and composition,

13.1.6 Pre-analysis purge time,

13.1.7 Number of determinations,

13.1.8 The weight percent highly volatile matter, medium volatile matter, combustible material, and ash content, and

13.1.9 Original (or photocopy) of the thermal curve.

### 14. Precision and Bias

14.1 *Precision*—On the basis of an interlaboratory test<sup>5</sup> of this test method, in which nine laboratories tested four materials on two days close together, using the test parameters in Table 1, the test results in Table 2 were obtained.

NOTE 3—The precision values stated in Table 2 are based on four specific materials studied in this interlaboratory test. These precision values may vary with the type of material analyzed and the testing parameters selected.

14.2 The interpretation of this data will produce individual precision statements for each material and component using the following as an example: two test results obtained by different laboratories on replicate samples of lubricating oil of about 2.5 % combustible material would not be expected to differ by more than 0.5 %.

14.3 *Bias*—No reference materials were selected for the interlaboratory testing of this test method, however data was provided for coal using Method D 3172 for proximate analysis. In addition, the results from the calcium oxalate compositional analysis can be compared to calculated theoretical values for each mass loss plateau. The bias indicated for this method is summarized in Table 3.

<sup>5</sup> Supporting data available from ASTM. Request RR: 1009.

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# **VOP METHOD PROCEDURE:**

## **Direct Measurement of Volatile Organics in Liquid Pesticide Formulations**

### **1. SCOPE**

The proposed method has been evaluated using commercially available pesticides sold as emulsifiable concentrates. The eleven solvent-based pesticides used in the evaluation had measured volatile organic (VO) content in the range 11-69% by weight and nonvolatiles in the range 28-88%. Two water-based pesticides were also analyzed.

Methanol, if present in the pesticide, will not be measured with other VO's since methanol is not adsorbed well by charcoal. Typically, a small amount of methanol will not be purged from the second charcoal tube. Methanol that is purged from the charcoal is trapped by the Drierite. Ethanol, if present, will be collected primarily on the first charcoal tube with the second charcoal tube collecting approximately 30% of the total.

### **2. SUMMARY OF TEST METHOD**

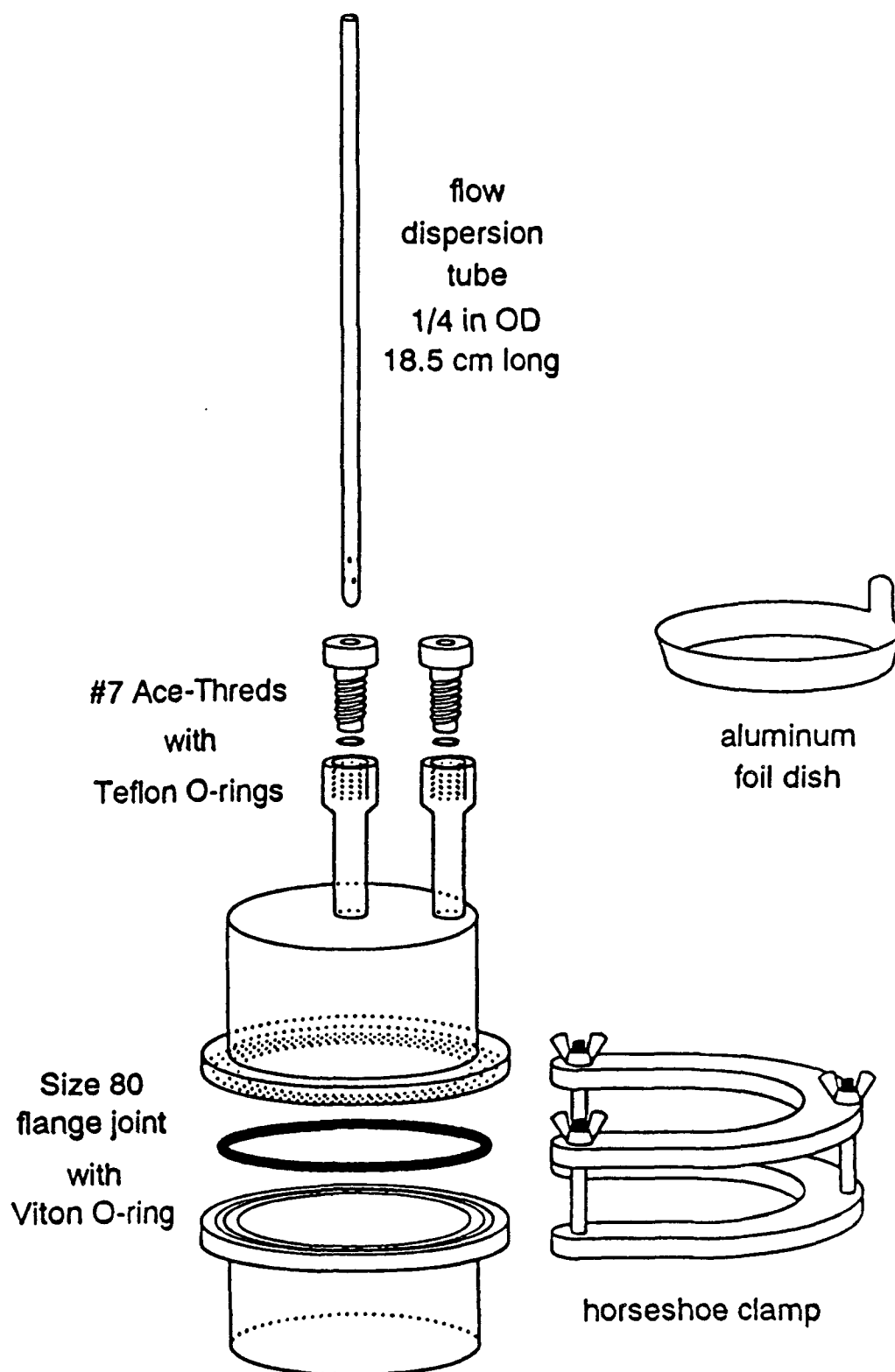
The proposed method involves purging volatiles from a weighed sample of liquid pesticide with dry nitrogen at 54°C, adsorption of VO in the volatile fraction onto activated charcoal in pre-weighed tubes, determination of final weights for both the pesticide residue and the charcoal tubes, and computation of weight percent of VO in the original pesticide. Water content may also be measured directly by trapping water from the stripped volatile stream emerging from the second charcoal tube on a dessicant (e.g., anhydrous  $\text{CaSO}_4$  or Drierite). Mass balance can be demonstrated by determining the weights of nonvolatiles (pesticide residue), VO, and water after heating, taking the sum of the three measurements, and comparing the result to the weight of the original pesticide sample.

### **3. SIGNIFICANCE AND USE**

This gravimetric test method allows direct measurement of the VO content of liquid pesticides. It also allows the direct measurement of nonvolatiles and water in pesticides. This method cannot differentiate between volatile active ingredient(s) and other VO present in the pesticide. However, speciation could be accomplished by desorption of the charcoal, analysis of the desorption solution by gas chromatography with mass spectrometric detection (GC-MSD), identification of the compounds present by library matching of the mass spectra, and quantification by means of appropriate standards.

### **4. APPARATUS**

**4.1 Volatilization Chamber**, shown schematically in Figure 1, is custom-made from 80 mm



**FIGURE 1. VOLATILIZATION CHAMBER**



OD (75 mm ID) glass tubing with a size 80 flange joint. The lower section is approximately 5 cm high and has a planar bottom. The upper section has two vertical #7 Ace-Thred connectors: one in the center (N<sub>2</sub> inlet) and one near the side (N<sub>2</sub> outlet). Use a Viton O-ring to seal the two sections of the chamber and a flange joint clamp to hold them firmly together. The N<sub>2</sub> inlet tube is a 7/4-in long by 1/4-in OD glass tube, sealed at the lower end, but with eight 1-mm holes around the tube 1/4 to 1/2 in above the sealed end. The holes disperse the purge gas laterally and prevent spattering of the pesticide. The outlet tube is 1/4-in OD Teflon tubing. The inlet and outlet tubes of the chamber are attached with #7 Ace-Thred connectors with Teflon O-rings. Adjust the height of the N<sub>2</sub> inlet tube so that its lower end is approximately 1/2 in from the bottom of the chamber.

**4.2 Aluminum Foil Dish** is 75 mm in diameter by 15 mm high with a planar bottom surface. Precondition aluminum foil dishes in an oven for 30 min at 120°C and store them in the oven (or in a dessicator) prior to use.

**4.3 Charcoal Tube**, shown schematically in Figure 2, is 18 cm long glass tube with 3.5 cm lower portion 1/4-in OD, 12.5 cm middle section 16-mm OD (14-mm ID), and a #7 Ace Thred connector on upper end, packed with activated charcoal. Wash tubes. Place a plug of glass wool in the tube near the lower, narrow end. Add  $5 \pm 1$  g activated charcoal into the upper end. Place a second plug of glass wool in the tube so that the charcoal is held firmly between the two plugs. Prepare two charcoal tubes for each pesticide sample to be run. Condition the unsealed charcoal tubes for 12 hours in an oven at 175°C. Remove the charcoal tubes from the oven and seal the ends with coded #7 Ace Thred plugs and end caps (for 1/4-in OD end). Allow the tubes to cool with plugs and end caps in place. Do not heat the #7 Ace Thred plugs or the plastic end caps.

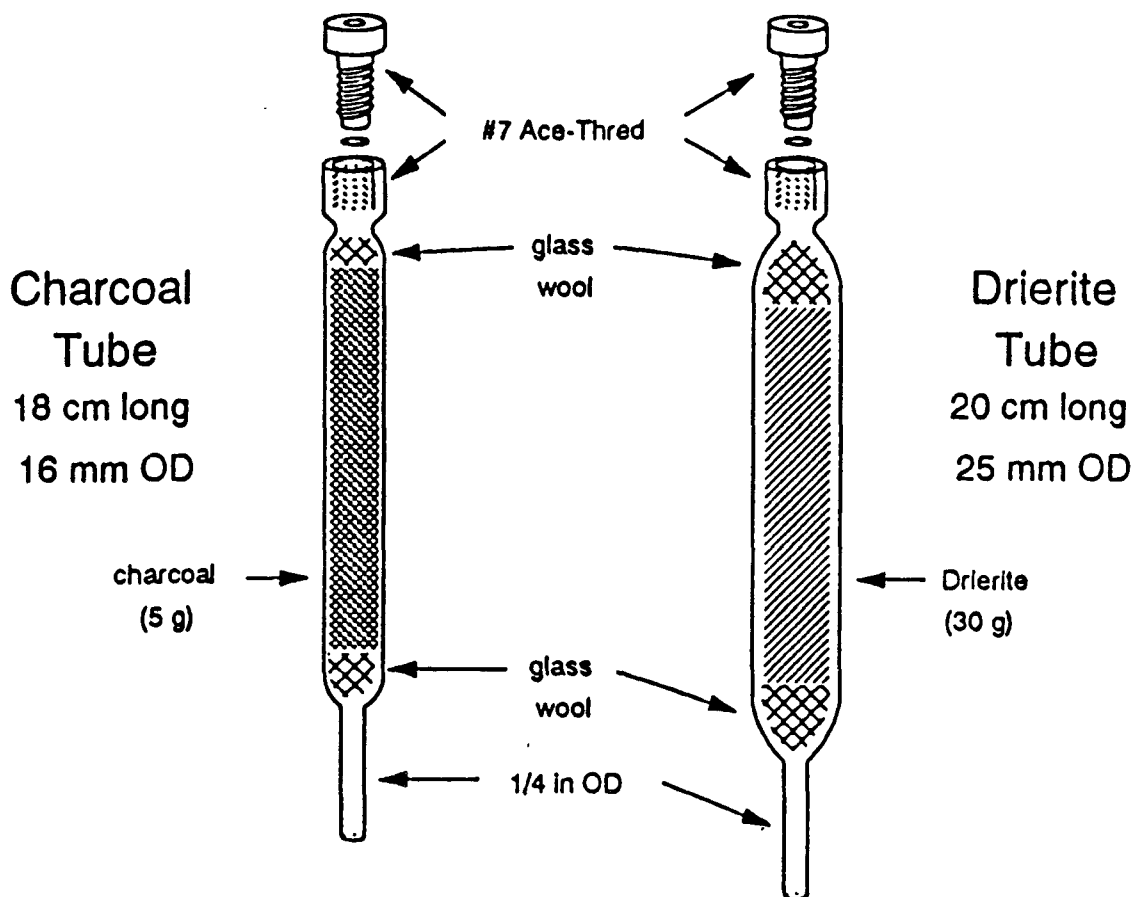
**4.4 Drierite Tube**, shown schematically in Figure 2, is 20 cm long glass tube with 3.5 cm lower portion 1/4-in OD, 14.5 cm middle section 25-mm OD (23-mm ID), and a #7 Ace Thred connector on upper end, packed with anhydrous indicating Drierite. If indicating Drierite contains any pink granules, heat it in an oven at 175°C until it is uniformly blue (anhydrous). Wash collection tubes and dry them in an oven. Place a plug of glass wool in the tube near the lower, narrow end. Add  $30 \pm 3$  g anhydrous indicating Drierite into the upper end. Place a second plug of glass wool in the tube so that the Drierite is held firmly between the two plugs. Prepare two Drierite tubes for each pesticide sample to be run. Seal the ends of the Drierite tubes with coded #7 Ace Thred plugs and end caps (for 1/4-in OD end) as they are removed from the oven. Allow tubes to cool with plugs and end caps in place. Drierite may be reused if heated as described above. Do not heat the #7 Ace Thred plugs or the plastic end caps.

**4.5 Oven**, gravity convection oven with ports added for inlet and outlet nitrogen lines.

**4.6 Union Elbow**, stainless steel Swagelok union elbow with teflon ferrules.

**4.7 Union Tee**, stainless steel Swagelok union tee with teflon ferrules.

**4.8 Flange Joint Clamp**, horseshoe style for flange joint size 80.



**FIGURE 2. COLLECTION TUBES**

## **5. REAGENTS**

**5.1 Activated Charcoal**, 6-14 mesh (Fisher Scientific, 3315 Atlantic Avenue, Raleigh, NC 27604; catalog number 05-685A).

**5.2 Indicating Drierite**, 8 mesh anhydrous  $\text{CaSO}_4$  (W. A. Hammond Drierite Company, Xenia, OH 45385).

## **6. PROCEDURE**

**6.1 Initial Set-up.** Procedures described in Sections 6.1.1 and 6.1.2 must be done before any samples are analyzed. Nitrogen flow rates and oven temperature should then be checked (and readjusted, if necessary) at the beginning of each analysis.

**6.1.1 Set Nitrogen Flow Rates.** Provide for two dry-nitrogen supply lines to the apparatus. Both lines should be 1/4-OD tubing, preferably made of teflon for flexibility. One line will supply  $\text{N}_2$  to the inlet of the volatilization chamber inside the oven, the other will supply  $\text{N}_2$  to the union tee in the outlet line just outside the oven. Nitrogen supplied through the by-pass line is not heated and thus lowers the temperature of the first charcoal tube and decreases the potential for breakthrough of VO. The additional  $\text{N}_2$  flow from the by-pass line

also facilitates the removal of water from the second charcoal tube. With a bubble flowmeter, adjust the  $N_2$  flow through the line to be attached to the chamber inlet to  $1.0 \pm 0.1$  L/min. In the same fashion, adjust  $N_2$  flow through the bypass line to be attached to the union tee to  $2.0 \pm 0.1$  L/min.

**6.1.2 Set Oven Temperature.** Assemble and seal an empty volatilization chamber in the oven (as shown in Figure 3, but do not attach the union tee or collection tube assembly). Attach a bubble flowmeter to the nitrogen outlet line from the chamber where it exits the oven. Adjust  $N_2$  flow through the chamber to 1 L/min. Remove the bubble flowmeter. Run a thermocouple down into the chamber through the teflon  $N_2$  outlet line. Position the thermocouple so that it is very near but not touching the bottom of the volatilization chamber. Adjust the temperature of the oven until the temperature inside the chamber remains at  $54 \pm 2^\circ\text{C}$  for 1 hour. Record the temperature of the oven and the control setting required to give a temperature of  $54 \pm 2^\circ\text{C}$  inside the volatilization chamber. The oven should be set at this temperature setting during subsequent pesticide analyses.

**6.2 Analysis.** Procedures described in Sections 6.2.1 through 6.2.11 must be done for each analysis. At least three replicate analyses should be performed on each pesticide.

**6.2.1** With a bubble flowmeter, check the nitrogen flow through the bypass line to confirm that it is  $2.0 \pm 0.1$  L/min. In the same fashion, check the nitrogen flow through the chamber to confirm that it is  $1.0 \pm 0.1$  L/min. If either flow rate is outside the given range readjust it as described in Section 6.1.1. Record the measured flow rates.

**6.2.2** Measure the temperature inside the oven to confirm that it is within  $\pm 5^\circ\text{C}$  of the oven temperature measured in Section 6.1.2. If the temperature is outside this range, readjust it as described in Section 6.1.2. Record the measured temperature.

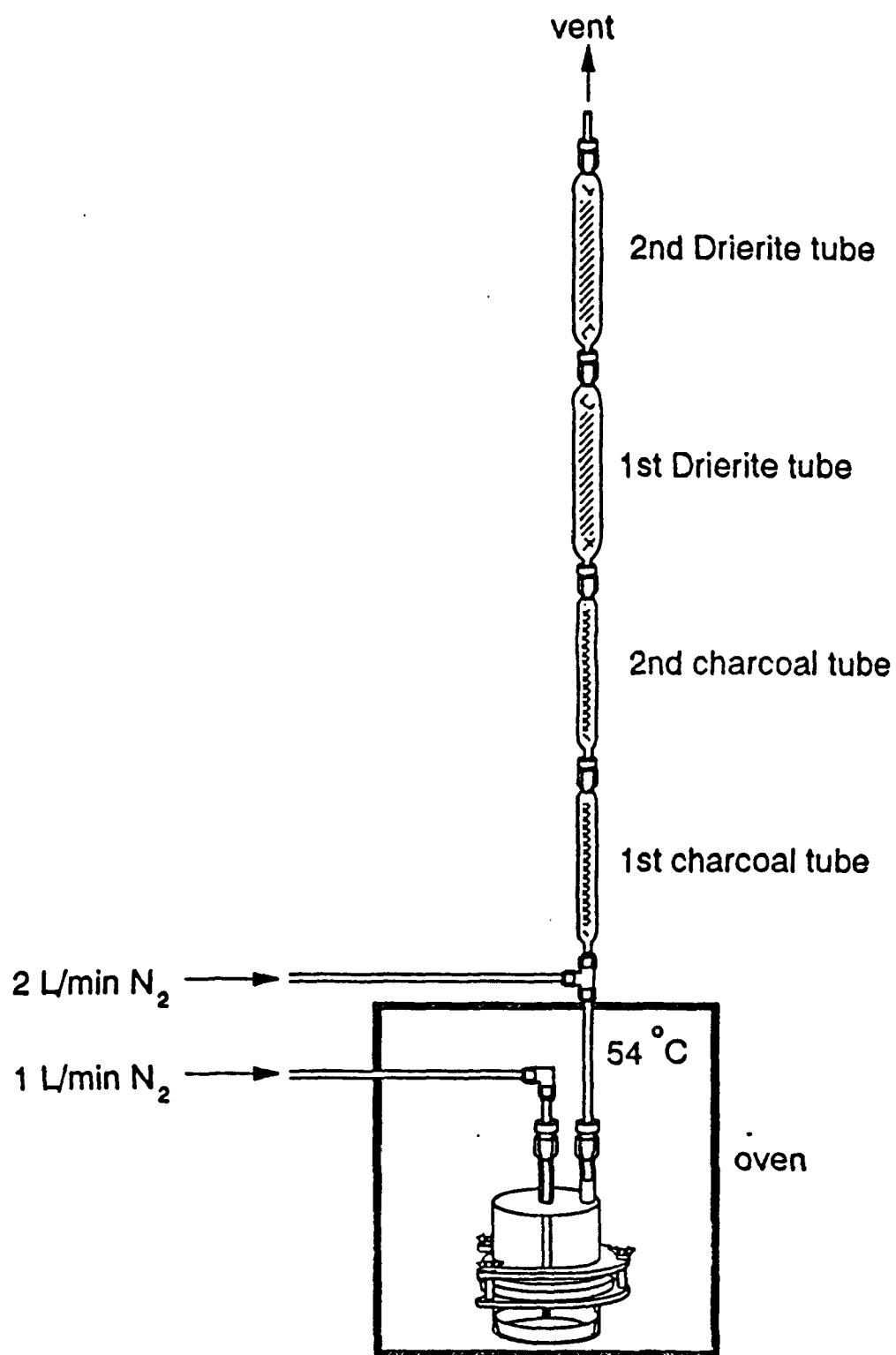
**6.2.3** Mix the pesticide until it is homogeneous.

**6.2.4** Label and weigh separately two charcoal tubes and two Drierite tubes to 0.1 mg. Tubes should be sealed before they are weighed. Record the weights.

**6.2.5** Refer to Figure 3. Attach the two charcoal tubes in series and the two Drierite tubes in series. With  $N_2$  flows off, attach the first charcoal tube to the union tee in the outlet line just outside the oven. Attach the first Drierite tube to the second charcoal tube.

**6.2.6** Weigh an aluminum foil dish to 0.1 mg and record the weight. Add  $1.0 \pm 0.1$  g of pesticide to the dish, weigh it to 0.1 mg, and record the weight. The weighing of the pesticide and the transfer of the dish to the volatilization chamber must be done quickly to avoid loss of volatiles.

**6.2.7** Quickly place the aluminum foil dish into the volatilization chamber, place the large O-ring between the top and bottom sections of the chamber, and place #7 Ace Thred plugs in the  $N_2$  inlet and outlet ports. Use the flange joint clamp to obtain an air-tight seal between the two sections of the chamber.



**FIGURE 3. ASSEMBLED APPARATUS**

**6.2.8** Place the volatilization chamber containing the aluminum foil dish in the oven. Remove the stopper from the #7 Ace Thread in the center of the top section of the chamber and install the nitrogen dispersion tube. Remove the remaining stopper and attach the N<sub>2</sub> inlet and outlet lines as shown in Figure 2.

**6.2.9 Leak Check.** With the apparatus fully assembled, measure the leak rate by attaching a water-filled manometer (or a 24-in loop of clear plastic tubing with water in the bottom 1/3 of the loop) to the outlet of the second Drierite tube. Allow just enough N<sub>2</sub> into the system to displace the water in the manometer by 3 ± 1 in. With both N<sub>2</sub> flows off, measure with a stopwatch the time required for the difference in water level on the two sides of the manometer to be reduced by 2 in or measure the change in difference in water level after 1 min, whichever comes first. Calculate the leak rate of the apparatus according to Equation 1.

$$\text{leak rate} = \frac{\pi d^2 c}{8t}$$

Eq. 1

d = ID of manometer tube (cm)

c = change in difference of water levels (cm)

t = time (min)

If the leak rate is 4 mL/min or less, continue with the next section of the procedure. If the leak rate is greater than 4 mL/min but less than 20 mL/min, tighten all connectors and measure the leak rate again. If the initial leak rate is 20 mL/min or greater, or if all leak problems are not solved within 5 min after placing the chamber in the oven, discard the pesticide sample and start over with a fresh one.

**6.2.10** Turn on the nitrogen gas flows through both the bypass inlet and the volatilization flask inlet. Measure the flow to insure that the outlet flow equals the sum of the two inlet flow rates measured in 6.2.1. Leave the apparatus in the oven at 54 ± 2°C with N<sub>2</sub> flowing for four hours.

**6.2.11** Turn off the N<sub>2</sub> flows and disassemble the apparatus. Replace the coded caps on the ends of the collection tubes. Weigh the cooled charcoal tubes (separately), the Drierite tubes, and the aluminum foil dish (containing the nonvolatiles) to 0.1 mg. Record these weights.

## 7. CALCULATIONS

Weight of the original pesticide sample, the nonvolatiles remaining after heating, the weight of VO collected on each charcoal tube, and the weight of water collected on each Drierite tube are calculated by difference. The weight of VO collected on the second charcoal tube typically should not be more than 10% of the weight of VO collected on the first charcoal tube. If it is more than 10%, either there has been breakthrough of some poorly sorbed VO (e.g., methanol) or water has not been completely purged from the second charcoal tube. In either event the results are invalid.

**7.1 Weight of Original Pesticide Sample.** The weight of the aluminum foil dish plus the

pesticide minus the weight of the empty aluminum foil dish (Section 6.2.6) gives the weight of the pesticide sample taken for analysis.

**7.2 Weight of Nonvolatiles.** The weight of the aluminum foil dish with the pesticide residue after heating (Section 6.2.11) minus the weight of the empty aluminum foil dish (Section 6.2.6) gives the weight of nonvolatiles in the pesticide sample taken for analysis.

**7.3 Weight of Volatiles.** The weight of the aluminum foil dish with the original pesticide sample (Section 6.2.6) minus the weight of the aluminum foil dish with the pesticide residue after heating (Section 6.2.11) gives the weight of volatiles in the pesticide sample taken for analysis.

**7.4 Weight of VO.** Weight of a charcoal tube after the heating step (Section 6.2.11) minus the weight of the same charcoal tube before the heating step (Section 6.2.4) gives the weight of VO collected on that charcoal tube. Calculate the weight gain of each charcoal tube separately to determine if breakthrough occurred as described above, then add the two weight gains to get total weight of VO in the pesticide sample taken for analysis.

**7.5 Weight of Water.** Weight of a Drierite tube after the heating step (Section 6.2.11) minus the weight of the same Drierite tube before the heating step (Section 6.2.4) gives the weight of water collected on that Drierite tube. Calculate the weight gain of each Drierite tube separately, then add the two weight gains to get total weight of water in the pesticide sample taken for analysis.

**7.6 Calculation of Weight Percent Nonvolatiles (%Nonvol):**

$$\% \text{Nonvol} = \frac{(\text{weight of pesticide residue after heating})}{(\text{weight of original pesticide sample})}(100) \quad \text{Eq. 2}$$

**7.7 Calculation of Weight Percent Volatiles (%Vol):**

$$\% \text{Vol} = \frac{(\text{weight lost by pesticide sample during heating})}{(\text{weight of original pesticide sample})}(100) \quad \text{Eq. 3}$$

**7.8 Calculation of Weight Percent VO (%VO):**

$$\% \text{VO} = \frac{(\text{total weight gained by the two charcoal tubes})}{(\text{weight of original pesticide sample})}(100) \quad \text{Eq. 4}$$

### 7.9 Calculation of Weight Percent Water (%H<sub>2</sub>O):

$$\%H_2O = \frac{(\text{total weight gained by the two Drierite tubes})}{(\text{weight of original pesticide sample})}(100) \quad \text{Eq. 5}$$

### 7.10 Calculation of Mass Balance Total (%TOT):

$$\%TOT = \%Nonvol + \%VO + \%H_2O \quad \text{Eq. 6}$$

The sum of %Nonvol, %VO, and %H<sub>2</sub>O should be 100 ± 5%.

## 8. PRECISION AND BIAS

8.1 Relative standard deviation (RSD) of VO content, as a rule, should be less than 10% for solvent-based pesticides.

8.2 Absolute bias has not been determined. In measurements of nonvolatile content of eleven pesticides, this method gave results that were equivalent, at the 95% confidence level, to those obtained by thermogravimetric analysis.





• APPENDIX D

OPP INERT INGREDIENTS POLICY STATEMENT



[OPP-36140A; FRL 3687-6]

**Inert Ingredients in Pesticide Products;  
Policy Statement; Revision and  
Modification of Lists**

**AGENCY:** Environmental Protection  
Agency (EPA).

**ACTION:** Notice.

**SUMMARY:** EPA is revising and  
modifying previously published lists of  
inert ingredients in pesticide products  
that are of toxicological concern and  
require priority testing. EPA is also  
addressing the period of time allowed to  
exhaust stocks of old formulations.

**EFFECTIVE DATE:** The modified lists are  
effective on November 22, 1989.

**ADDRESSES:** Three copies of written  
comments bearing the document control  
number [OPP-36140A] should be  
submitted, by mail, to: Public Docket  
and Freedom of Information Section,  
Field Operation Division (H7504C),  
Office of Pesticide Programs,  
Environmental Protection Agency, 401 M  
St., SW., Washington, DC 20460.

In person, deliver comments to: Rm.  
246, CM #2, 1921 Jefferson Davis Hwy.,  
Arlington, VA.

Information submitted as a comment  
in response to this Notice may be

claimed confidential by marking any  
part or all of that information as  
"Confidential Business Information"  
(CBI). Information so marked will not be  
disclosed except in accordance with  
procedures set forth in 40 CFR part 2. A  
copy of the comment that does not  
contain CBI must be submitted for  
inclusion in the public docket.  
Information not marked "confidential"  
will be included in the public docket  
without further notice. The public  
docket is available for public inspection  
in room 246 at the address given above  
from 8 a.m. to 4 p.m., Monday through  
Friday, except legal holidays.

**FOR FURTHER INFORMATION CONTACT:**  
Lynn M. Bradley, Registration Support  
Branch, Registration Division (H7503C),  
Environmental Protection Agency, 401 M  
St., SW., Washington, DC 20460, (202)-  
703-557-7700.

**SUPPLEMENTARY INFORMATION:** EPA  
announced its policy on toxic inert  
ingredients in pesticide products in the  
Federal Register of April 22, 1987 (52 FR  
13305). Through this policy, EPA  
encourages the use of the least toxic  
inert ingredients available and requires  
the development of data necessary to  
determine the conditions of safe use of  
products that contain toxic inert  
ingredients. In developing this policy,  
EPA categorized inert ingredients into  
the following four lists according to  
toxicity:

- List 1 Inerts of toxicological concern
- List 2 Potentially toxic inerts, with high  
priority for testing
- List 3 Inerts of unknown toxicity
- List 4 Inerts of minimal concern

List 1 and List 2 were published as  
part of the April 22, 1987 policy  
statement.

The criteria developed by EPA to  
categorize List 1 inerts were reviewed  
by the Federal Insecticide, Fungicide,  
and Rodenticide Act's Scientific  
Advisory Panel (FIFRA SAP). Chemicals  
were placed on the list of inerts of  
toxicological concern if they met any  
one of the following criteria.

(1) Carcinogenicity:

- A rating as a human carcinogen of  
probable human carcinogen (rating 1,  
2A or 2B) by International Agency for  
Research on Cancer.
- Characterized by the National  
Toxicology Program as an animal  
carcinogen in at least one species and  
one sex.

- Being regulated by some Federal agency as a carcinogen.
- (2) Neurotoxicity and other Chronic Effects:
  - Identified in the Occupational Diseases, a Guide to their Recognition (1977), as causing neurotoxicological and other chronic effects in the workplace environment.
  - Being regulated by some Federal agency as a neurotoxin.
  - Peer reviewed study, included in the Toxicology Data Bank of the National Library of Medicine, reporting neurotoxic or other chronic effects.
- (3) Adverse Reproductive Effects:
  - Being regulated by some Federal agency as causing adverse reproductive effects.
  - Peer reviewed study, included in the Toxicology Data Bank of the National Library of Medicine, reporting adverse reproductive effects.
- (4) Ecological Effects:
  - An LC50 of less than one part per million.

#### Revision of Lists of Inert Ingredients

Since the publication of the policy, EPA has received additional data on some of the listed inerts. EPA scientists have reviewed this information according to criteria previously developed and used in the creation of the initial lists. As a result of this recent examination of new data, EPA proposed modifications to the lists. These modifications were submitted to the FIFRA SAP for review. The FIFRA SAP concluded that the proposed changes were justified.

EPA is announcing the following revised List 1 and List 2.

#### LIST 1.—INERTS OF TOXICOLOGICAL CONCERN

CAS No.	Chemical name
62-53-3	Aniline
1332-21-4	Asbestos fiber
1332-21-9	1,4-Benzenediol
7440-43-9	Cadmium compounds
58-23-5	Carbon tetrachloride
67-66-3	Chloroform
106-46-7	p-Dichlorobenzene
103-23-3	Di-(2-ethylhexyl)adipate
78-67-5	1,2-Dichloropropane
117-87-8	Di-ethylhexylphthalate
68-12-2	Dimethylformamide
123-91-1	Dioxane
106-88-6	Epichlorohydrin
110-80-5	2-ethoxyethanol
111-15-9	Ethanol ethoxyacetate
107-06-2	Ethylene dichloride
109-86-4	Ethylene glycol monomethyl ether
140-88-5	Ethyl acrylate
110-54-3	n-Hexane
302-01-2	Hydrazine
78-59-1	Isononane
7439-92-1	Lead compounds
588-84-2	Malachite green
591-78-6	Methyl n-butyl ketone

#### LIST 1.—INERTS OF TOXICOLOGICAL CONCERN—Continued

CAS No.	Chemical name
74-87-3	Methyl chloride
75-09-2	Methylene chloride
25154-52-3	Nonylphenol
127-18-4	Perchloroethylene
106-95-2	Phenol
90-43-7	o-Phenylphenol
75-58-9	Propylene oxide
8003-34-6	Pyrethrin
81-88-9	Rhodamine B
10588-01-9	Sodium dichromate
26471-82-5	Toluene diisocyanate
79-00-5	1,1,2-Trichloroethane
56-35-9	Tributyl tin oxide
79-01-6	Trichloroethylene
1330-78-3	Tri-orthocresylphosphate (TOCP)
78-30-8	Tri-orthocresylphosphate (TOCP)

#### LIST 2.—POTENTIALLY TOXIC INERTS/ HIGH PRIORITY FOR TESTING

CAS No.	Chemical name
85-88-7	Butyl benzyl phthalate
84-74-2	Dibutyl phthalate
84-66-2	Diethyl phthalate
131-11-3	Dimethyl phthalate
117-84-0	Diethyl phthalate
95-49-8	2-Chlorotoluene
1319-77-3	Cresols
95-48-7	o-Cresol
106-44-5	p-Cresol
106-39-4	m-Cresol
106-84-1	Cyclohexanone
95-50-1	o-Dichlorobenzene
112-34-5	Diethylene glycol monobutyl ether
111-90-0	Diethylene glycol monoethyl ether
111-77-3	Diethylene glycol monomethyl ether
34560-84-8	Dipropylene glycol monomethyl ether
111-76-2	2-Butoxy-1-ethanol
5131-86-8	1-Butoxy-2-propanol
124-16-3	1-Butoxyethoxy-2-propanol
107-98-2	1-Methoxy-2-propanol
29387-86-8	Propylene glycol monobutyl ether
25498-48-1	Tripropylene glycol monomethyl ether
141-78-7	Mesityl oxide
106-10-1	Methyl isobutyl ketone
96-23-7	Methyl ethyl ketoxime
106-80-7	Monochlorobenzene
75-52-6	Nitromethane
106-88-3	Toluene
29396-43-1	Tolyl triazole
95-14-7	1,2,3-Benzotriazole
120-32-1	2-Benzyl-4-chlorophenol
75-00-3	Chloroethane
88-04-0	p-Chloro-m-xylene
97-23-4	Dichlorophene
100-41-4	Ethyl benzene
149-30-4	Mercaptobenzotriazole
74-83-6	Methyl bromide
75-43-4	Chlorodifluoromethane
75-43-4	Dichloromonofluoromethane
75-45-6	Chlorodifluoromethane
75-37-6	1,1-Difluoroethane
75-68-3	1-Chloro-1,1-difluoroethane
25168-06-3	Isopropyl phenols Petroleum hydrocarbons
1330-20-7	Xylene
100-02-7	p-Nitrophenol
106-88-7	Butylene oxide
79-24-3	Nitroethane
75-05-6	Acetonitrile
71-55-6	1,1,1-Trichloroethane
102-71-6	Trichloroethylene
111-42-2	Diethanolamine

#### LIST 2.—POTENTIALLY TOXIC INERTS/ HIGH PRIORITY FOR TESTING—Continued

CAS No.	Chemical name
97-88-1	Butyl methacrylate
80-62-8	Methyl methacrylate Xylene-range aromatic solvents
95-82-9	2,5-Dichloroaniline
95-76-1	3,4-Dichloroaniline
626-43-7	3,5-Dichloroaniline
554-00-7	2,4-Dichloroaniline
608-27-5	2,3-Dichloroaniline
608-31-1	2,6-dichloroaniline
101-84-8	Diphenyl ether
78-13-1	Trichlorotrifluoroethane
75-69-4	Trichlorotrifluoroethane
75-71-8	Dichlorodifluoromethane
79-14-2	Dichlorotetrafluoroethane

The changes made and the reasons for the changes are explained below.

#### Additions to List 1

Di-(2-ethylhexyl)adipate and dimethyl-formamide (DMF) were moved to List 1 from Lists 3 and 2, respectively. Based on a National Toxicology Program bioassay, positive results for oncogenicity were indicated for di-(2-ethyl-hexyl)adipate: This chemical caused increased incidences of hepatocellular carcinomas in female mice, and thus meets one of the criteria for categorization as a List 1 inert.

For dimethylformamide (DMF), hepatotoxicity has been reported at very low doses in animal studies and is commonly observed in case reports of industrial exposure. Developmental toxicity has also been reported to occur in animal studies in the literature. In addition, recent reports of clusters of testicular cancer associated with human exposure to DMF have added to the weight of evidence which supports upgrading this compound from List 2 to List 1.

#### Additions to List 2

Based on data available at the time of the April 22, 1987, FR Notice, monochlorobenzene was determined to be an oncogen as well as an ecotoxin. For these reasons, it was placed on List 1. The EPA Science Advisory Board has reviewed the oncogenicity data on monochlorobenzene and concluded that it is a class D oncogen, i.e., not classifiable. EPA scientists have reevaluated the ecotoxicity data and concluded that monochlorobenzene does not meet List 1 ecotoxicity triggers. Because of these determinations, monochlorobenzene is being moved from List 1 to List 2 and is now considered as a high priority for testing.

Methyl ethyl ketoxime has been moved from List 3 to List 2 because of its close structural relationship to

acetoxime, which has been reported as being carcinogenic in preliminary tests and is also positive in a mouse lymphoma test. Methyl ethyl ketoxime has been proposed for testing under section 4 of the Toxic Substances Control Act.

#### Additions to Lists 3 and 4

To accommodate revision of the lists, EPA has decided to subdivide List 4 into two parts. The previous List 4, representing inerts generally regarded as safe, has become List 4A, and a new List 4B has been created. List 4B is composed of inerts for which EPA has sufficient information to reasonably conclude that the current use patterns in pesticide products will not adversely affect public health and the environment. List 4B inerts in formulations proposed for new use patterns which cause significant increases in exposure will receive further scrutiny.

Two inerts, gammabutyrolactone and dioctyl sodium sulfosuccinate (DSS), are being removed from List 2 because EPA now has a complete human health effects data base indicating that they do not meet the criteria for List 1 and that their current use in pesticides should not adversely affect human health.

The placement of gammabutyrolactone on List 2 was based on structural analogy to the known oncogen, betabutyrolactone. Further review indicates this analogy is inappropriate. In addition, a review of toxicity data for gammabutyrolactone, including acute and subchronic data, developmental toxicity, mutagenicity, and oncogenicity indicates a low order of toxicity. Thus EPA has decided to remove gammabutyrolactone from List 2 and add it to List 4B because current use patterns pose minimal risk for human health. Because gammabutyrolactone has not been adequately tested for ecotoxicity, however, it is being placed on List 3 for these effects. EPA decided to list the inert on two lists to reflect the different degree of knowledge the Agency has about the inert's various effects. EPA considered it appropriate to place the inert on List 4B because it has sufficient information about human health effects, and to also place it on List 3 to reflect inadequate information concerning the ecotoxicity of this inert.

DSS was placed on List 2 because of developmental and reproductive toxicity concerns as well as ecotoxicity concern for surfactants. Data have now been reviewed for these effects, and indicate a low order of toxicity. Thus, DSS is added to List 4B for nonadverse effects

on human health. Because of limited ecotoxicity testing, however, DSS remains on List 3 (unknown toxicity) for these effects.

#### Deletions From All Lists

Further investigation of ethylene thiourea, carbon disulfide, and 1, 1-dimethylhydrazine (UDMH, the impurity in Alar, which is in Special Review), has revealed that these are only impurities, not intentionally added inerts. Furthermore, betabutyrolactone, benzene, dichlorvos, 1, 2-dimethylhydrazine, pentachlorophenol and sodium pentachlorophenate, dinitro-*o*-cresol, dinitrophenol, ethyl methyl phenylglycidate, formaldehyde and paraformaldehyde, hexachlorophene, mercury oleate, 2-nitropropane, 1, 2-dichloropropane, and thiourea are not now used as inerts in any pesticide products. Therefore, these chemicals have been removed from all lists of inert ingredients and are not currently cleared for use as inerts in any pesticide product. Thus, in the event a registrant or applicant proposes to include one of these chemicals as an inert ingredient in a pesticide product, EPA will consider the chemical a new inert.

Impurities in registered products are contaminants from the manufacturing process for the active ingredient, rather than intentionally added inert ingredients. The presence and toxicity of impurities is routinely evaluated during the normal Agency review processes. Impurities are identified in the product chemistry review, and would probably have been present, as part of the test material, during testing considered for support of the registration. Thus, it is not appropriate to subject impurities to the Inerts Strategy.

As discussed in the April 22, 1987 Notice, registrants with products containing List 1 inert ingredients must amend their product registrations by adding the following statement to the label:

This product contains the toxic inert ingredient (name of inert).

The wording should be placed in close proximity to the ingredients statement in a type size comparable to other front panel text. Since dimethylformamide and di-(2-ethylhexyl) adipate have been added to List 1, registrants of products containing these inerts are required to submit applications to amend their product labels not later than May 22, 1990. Products containing one or more of these inert ingredients released for shipment after May 22, 1991 must have the amended label in place.

Registrants of products containing dimethylformamide have already received a Data Call-In. All registrants have either voluntarily cancelled or committed to reformulate the product. Most reformulations have been received; a few time extensions were granted to allow for necessary testing of the reformulated product.

A Data Call-In for di-(2-ethylhexyl) adipate will be issued, at the same time as for diethylhexylphthalate, since the uses are similar and we expect to find them in the same types of products. Data Call-Ins for other original List 1 inerts were mailed in March 1989.

#### Stocks of Old Formulations

Registrants are encouraged to substitute or remove any List 1 or List 2 inert ingredient from their products by submitting a new Confidential Statement of Formula as a proposed amendment to the registration. The April 22, 1987 Policy statement did not address provisions governing the sale of stock of old formulations. If a registrant reformulates its product to replace a List 1 or List 2 inert ingredient with a less toxic inert, EPA has determined that some limit on continued sale of stocks of the old formulation is appropriate.

Once a registrant submits the revised formulation, registrants may manufacture only the old formulation, properly labeled as containing a toxic inert as described above, until EPA accepts the new formulation. Stocks of the old formulation, bearing the required labeling, may be released for shipment by the registrant for a period not to exceed twelve months from the date EPA accepts the new formulation. Products already in channels of trade (retailers, distributors, dealers) are not subject to this limitation.

Dated: October 10, 1989.  
Douglas D. Campt,  
Director, Office of Pesticide Programs.  
[FR Doc. 89-27213 Filed 11-21-89; 8:45 am]  
BILLING CODE 5050-50-M

